

Chemistry of Tin

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Chemistry of Tin

SECOND EDITION

Edited by

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Preface

In common with the editor of the first edition, my own personal involvement with tin chemistry began when I had the privilege of studying for a PhD degree under the supervision of Professor Alwyn G. Davies FRS at University College London (UCL) almost exactly 30 years ago. Then, following 21 years' service with the International Tin Research Institute, it was a great pleasure for me when the wheel turned full circle and, in 1994, Alwyn – now an Emeritus Professor – asked me to return to UCL as an Honorary Research Fellow in the Chemistry Department.

One of my first tasks was when I received an invitation from Blackie A&P to edit the second edition of the *Chemistry of Tin*, which I was delighted to accept, since it enabled me to continued my life-long interest in tin chemistry and to maintain contact with my former friends and colleagues, many of whom have contributed to this book.

So, how does the second edition differ from the first? In this volume, which is addressed to academic researchers, analytical chemists and scientists in industry, there are six new chapters covering $^{119\text{m}}\text{Sn}$ Mössbauer studies; solid state NMR; use in organic synthesis; environmental analysis; biological properties; and health and safety aspects. Five chapters from the first edition have been rewritten and updated by their original authors, whilst the remaining four chapters retain essentially their original form. I had also planned to include a chapter on the chemistry and structure of tin complexes, but the author, Professor V. G. Kumar Das (University of Malaya), unfortunately suffered a period of ill-health and was unable to undertake his contribution. Happily, he has now fully recovered.

A number of books covering organotin compounds [1–5] have appeared since the first edition of the *Chemistry of Tin* and the on-going *Gmelin Handbuch der Anorganischen Chemie* has reached Part 23 of its supplements on organotin compounds. The triennial *International Conferences on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead* (ICCOC-GTL), which have contributed so much to bringing together the Group 14 interdisciplinary family of scientists, have continued in Brussels (1989), Riga (1992), Sendai (1995) and, in September 20–25, 1998, the venue for the 9th ICCOC-GTL will be Melbourne, Australia. I have been fortunate enough to attend and enjoy all but one of these meetings since their inception at Marseille in 1973, and look forward to many to come.

P.J. Smith

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1 Tin – the element

P.G. HARRISON

1.1 From earliest times

The discovery, around 3500 BC, that copper, easily smelted but rather soft, could be made harder and stronger by alloying with tin, can be considered to be one of the great milestones in man's technological development, and heralded the advent of the Bronze Age. Because of its relative scarcity, tin has always been a strategic metal and remains so to the present day. Isolation of the pure metal probably only dates from about 800 BC. The earliest recorded reference to tin occurs in the Old Testament in the book of Numbers (31:22): 'Only the gold, and the silver, the brass, the tin, and the lead.' Substantially later (c. 600 BC) Ezekiel (27:12) relates: 'Tarshish was thy merchant by reason of the multitude of all kind of riches; with silver, iron, tin, and lead, they traded in their fairs.' Both suggest that tin was regarded as a valuable commodity, and indeed a strip of tin free from silver and lead has been found in the wrappings of an Egyptian mummy dating from not later than 600 BC.

The Bronze Age of the ancient Western world not only represented the first production of a truly useful metal but also, because of its relative scarcity compared to copper, resulted in the development of substantial trading contact. Around 2000 BC, tin for the eastern Mediterranean could be obtained from Central Europe, and by 1800 BC trading links allowed bronze manufacture over much of the then known world. Knowledge of bronze is reputed to have travelled to other ancient civilizations, such as China, from the west, and the oldest Chinese bronze artefacts date from 2200 BC.

The early sources of tin are shrouded in uncertainty. The Greek chronicler Herodotus referred, around 440 BC, to 'the islands called the Cassiterides, from which we are said to have our tin'. The actual location of these islands has been the subject of much debate, and has been identified with various places including Cornwall, the Scilly Isles or supposed islands off the French coast, but gradually Spain, Britain and Brittany became known as the sources of tin. Not until 8 BC can Cornwall be definitely identified in Diodorus Siculus' *Bibliotheca historica*, although the Phoenicians may have worked tin mines in Cornwall as early as 1000 BC. Some confusion between tin and lead appears to have occurred in the ancient world. Pliny in his *Historia naturalis* writes:

There are two kinds of plumbum – nigrum and candidum or album [i.e. black lead and shining or white lead]. The plumbum candidum is the most valuable

and it was called *cassiteros* by the Greeks. There is a fabulous story told of their going in quest of it to the islands in the Atlantic Ocean. and of its being brought in boats made of osiers covered with hides. The *plumbum candidum* occurs as a black sand found on the surface of the earth, and is to be detected only by its weight, it is mingled with small pebbles, particularly in the dried beds of rivers. The miners wash the sand, which is then melted in the furnace and becomes converted into *plumbum album*.

Without doubt Pliny's *plumbum candidum* was tin and his *plumbum nigrum* lead. He further described Roman vessels made of copper and coated with *stannum*, and also states that *plumbum candidum* was esteemed even in the days of the Trojan War. Homer writes of it in the *Iliad* under the name of *cassiteros*.

The early Greek alchemists called tin 'Hermes', but by about AD 500 alchemists called it 'Zeus' or 'Jupiter', and represented it by the symbol Σ (derived from a corruption of the first and last letters of $\Sigma\epsilon\upsilon\varsigma$), which was understood to mean the thunderbolts of the king of the gods. It was also referred to as *diabulus metallorum*, the devil of metals, because of the embrittling effect it had on alloying with other metals. Geber, in his *Summa Perfectionis Magisterii*, probably written about the 12th century, writes: 'Of Jupiter or Tin. We Signifie to the Sons of Learning, the Tin is a Metallick Body, white, not pure [white], livid, and Sounding little, partaking of little Earthiness; Possessing in its Root Harshness, Softness, and Swiftness of Liquefaction, without ignition, and not abiding the Cupel, or Cement, but Extenssible under the Hammer. . . . Its vice is, that it breaks every [metallic] Body, but Saturn [lead], and most pure Sol [gold]' [i.e. when alloyed with them it makes them brittle].

Compounds of tin appear to date back to the Copts of Egypt, who reportedly used basic tin citrate in dye preparation. Modern chemistry of tin appears to start with the classic experiments of Libavius in 1605, who described a fuming liquid which he called *liquor argenti vivi sublimati* or *spiritus argenti vivi sublimati* prepared by distillation from a mixture of tin or tin amalgam and mercuric chloride. The liquid, obviously tin(IV) chloride, was thereafter referred to as *spiritus fumans Libavii*. It is possible, however, that the same experiment was carried some 300 years earlier! Although there are other reports originating in the 17th century, it was principally in the 18th century that inorganic tin compounds began to be studied in earnest. The first organotin compound, diethyltin diiodide, was prepared by Frankland in 1849, when tin chemistry came of age (for a relatively recent authoritative account see Ref. 1).

1.2 Occurrence

Important tin-producing countries are Malaysia, Bolivia, Indonesia, Nigeria, Thailand, Zaire and China, with smaller quantities from the United

Kingdom, Burma, Japan, Canada, Portugal, Spain and Australia. By far the most important ore, and the only one of major commercial importance, is cassiterite, a naturally occurring form of tin(IV) oxide. Other ores are sulphidic in nature and include stannite, $\text{SnS}_2 \cdot \text{Cu}_2\text{S} \cdot \text{FeS}$; herzenbergite, SnS ; teallite, $\text{SnS} \cdot \text{PbS}$; franckeite, $2\text{SnS}_2 \cdot \text{Sb}_2\text{S}_3 \cdot 5\text{PbS}$, cylindrite, $\text{Sn}_6\text{Pb}_6\text{Sb}_2\text{S}_{11}$; plumbostannite, $2\text{SnS}_2 \cdot 2\text{PbS} \cdot 2(\text{Fe}, \text{Zn})\text{S} \cdot \text{Sb}_2\text{S}_3$; and canfieldite, $4\text{Ag}_2\text{S} \cdot \text{SnS}_2$. These ores are of commercial significance only in Bolivia.

1.3 Physical properties of metallic tin

Tin has the largest number (10) of stable isotopes of any element, and in addition many unstable isotopes with half-lives varying from 2.2 min to $\sim 10^5$ years (Tables 1.1 and 1.2) The normal form of the element is β - or white tin, but α -

Table 1.1 Stable isotopes of tin

	Mass	Abundance (%)
^{112}Sn	111.90494	0.95
^{114}Sn	113.90296	0.65
^{115}Sn	114.90353	0.34
^{116}Sn	115.90211	14.24
^{117}Sn	116.90306	7.57
^{118}Sn	117.90179	24.01
^{119}Sn	118.90339	8.58
^{120}Sn	119.90213	32.97
^{122}Sn	121.90341	4.71
^{124}Sn	123.90524	5.98

Table 1.2 Unstable isotopes of tin

	Half-life	Mode of decay	Decay energy (MeV)
^{108}Sn	9 min	EC	
^{109}Sn	18.1 min	β^+ , EC	
^{110}Sn	4.0 h	EC	
^{111}Sn	35 min	β^+ , EC	2.52
$^{113\text{m}}\text{Sn}$	20 min	IT, EC	0.079, 1.1
^{113}Sn	115 d	EC	1.02
$^{117\text{m}}\text{Sn}$	14 d	IT	0.317
$^{119\text{m}}\text{Sn}$	250 d	IT	0.089
$^{121\text{m}}\text{Sn}$	76 years	β^-	0.45
^{121}Sn	27 h	β^-	0.383
$^{123\text{m}}\text{Sn}$	125 d	β^-	1.42
^{123}Sn	42 min	β^-	1.46
$^{125\text{m}}\text{Sn}$	9.7 min	β^-	2.39
^{125}Sn	9.4 d	β^-	2.34
^{126}Sn	$\sim 10^5$ years	β^-	-0.3
$^{127\text{m}}\text{Sn}$	4 min	β^-	-3.1
^{127}Sn	2.1 h	β^-	
^{128}Sn	59 min	β^-	1.3
^{130}Sn	2.6 min		
^{131}Sn	3.4 min		
^{132}Sn	2.2 min		

or grey tin is the thermodynamically stable modification below 13.2°C. The existence of a third form referred to as γ -tin and said to be stable at temperatures in excess of 161°C has not been substantiated. Physical, crystallographic, thermal and spectroscopic data for elemental tin are collated in Tables 1.3–1.7. The β -form of tin is a silvery-white metal which is relatively soft and ductile, and can emit a characteristic cracking noise when subjected to stress deformation (the so-called ‘cry’ of tin) due to plastic deformation along the [301] crystal twinning plane. Transformation from the β - to the α -form is quite slow and does not proceed at an appreciable rate except at temperatures of *c.* –40°C. The transformation of tin into the grey form under extreme of cold was first observed by Aristotle, and came to be known as ‘tin pest’ or ‘tin disease’. When tin or a tin alloy is affected by tin pest, grey-coloured spots appear and the metal becomes brittle. Because of the large density change, the metal expands, producing pustule-like or nodular excrescences at the affected points. Transformation extends radially outward from the spots until the whole mass is infected. The metal then breaks down and disintegrates to a brittle powder. The change can be retarded or even inhibited by the presence of trace amounts of impurity metals such as aluminium, zinc, antimony or bismuth. The two modifications have quite different structures, which accounts for many of the differences in their properties. Thus, β -tin is a typical metallic conductor (though much poorer than copper), whereas, in contrast, α -tin exhibits high resistivity and is semiconducting.

The α -form has the diamond structure, with each tin atom having four nearest neighbours at 280 pm. The structure of β -tin is much less symmetrical and is related to that of α -tin in an interesting way. In Figure 1.1a the α -tin

Table 1.3 Physical properties of tin

Property		Value
Density		
α -Tin	(measured at 288 K)	7.29 g cm ⁻³
	(from X-ray at 299 K)	7.2867 ± 0.0024 g cm ⁻³
β -Tin	(measured at 288 K)	5.77 g cm ⁻³
	(from X-ray at room temperature)	5.765 g cm ⁻³
Liquid	(measured at m.p.)	6.968 ± 0.005 g cm ⁻³
		6.978 ± 0.022 g cm ⁻³
	(measured at 600 K)	6.70 g cm ⁻³
	(measured at 1200 K)	6.29 g cm ⁻³
Hardness	(Moh scale)	1.5–1.8
	(at 293 K)	3.9 HB
	(at 373 K)	2.3 HB
	(at 473 K)	0.9 HB
Resistivity		
α -Tin	(at 293 K)	12.6 $\mu\Omega$ cm
β -Tin	(at 273 K)	300 $\mu\Omega$ cm
Young's modulus	(at 293 K)	49.9 kN mm ⁻²
Bulk modulus	(at 293 K)	58.2 kN mm ⁻²
Shear strength	(room temperature)	12.3 N mm ⁻²

Table 1.4 Crystallographic data

α -Tin	Crystal system	Cubic
	Space group	Fd3m (type A4)
	<i>Z</i>	2
	<i>a</i>	64.912 ± 0.005 pm
	Nearest-neighbour distances	4 at 280 pm
		12 at 459 pm
	Lattice <i>d</i> -spacings (relative intensities in parentheses)	37.3(100) pm
		22.8(80) pm
		19.5(70) pm
		16.1(30) pm
		14.8(50) pm
		13.2(60) pm
		12.4(40) pm
		11.4(20) pm
β -Tin	Crystal system	Tetragonal
	Space group	14 ₁ /amd(141)
	<i>Z</i>	4
	<i>a</i> (299 K)	58.315 ± 0.008 pm
	<i>c</i> (299 K)	31.813 ± 0.006 pm
	Cell volume (299 K)	108.18 ± 0.04 × 10 ²⁴ cm ⁻³
	Nearest-neighbour distances	4 at 302 pm
		2 at 318 pm
		4 at 377 pm
		8 at 441 pm
	Twinning plane	(301)
	Lattice <i>d</i> -spacings (relative intensities in parentheses)	29.153(100) pm
		27.93(90) pm
		20.62(34) pm
		20.17(74) pm
		16.59(17) pm
		14.84(23) pm
		14.58(13) pm
		14.42(20) pm
		13.04(15) pm
		12.92(15) pm
		12.05(20) pm
		10.95(13) pm

structure is shown referred to a tetragonal unit cell (*a* axes at 45° to the axes of the conventional cubic unit cell). In the diamond structure, the six inter-bond angles are equal (109.47°), but in β -tin the coordination tetrahedron is severely flattened so that two of these angles are enlarged to 149.5° while the other four are reduced to 94° (Figure 1.1b). In this process, the nearest neighbours change from four at 280 pm in α -tin to four at 302 pm and a further two at 318 pm, and coordination of tin in the β -modification is best regarded as distorted octahedral (Figure 1.1c). This structural change is remarkable, not only because of the 26% increase in density (causing the phenomenon known as ‘tin pest’), but also because the more dense β -tin modification is the high-temperature form. The relationship between the two forms has been discussed at length [2]. The transformation between the two modifications is

Table 1.5 Thermal data

Fusion point	231.9681 °C
Enthalpy of fusion	7.06 kJ atom ⁻¹
Entropy of fusion	3.35 e.u.
Boiling point	2270 °C
Enthalpy of vaporization	296.4 kJg atom ⁻¹
Vapour pressure	
at 1096 K	10 ⁻⁵ mm Hg
at 1196 K	10 ⁻⁴ mm Hg
at 1315 K	10 ⁻³ mm Hg
at 1462 K	10 ⁻² mm Hg
at 1646 K	10 ⁻¹ mm Hg
at 1882 K	1 mm Hg
Entropy at 295 K	12.3 e.u.
Specific heat (C _v) at 298 K	
α-Tin	215.5 J kg ⁻¹ K ⁻¹
β-Tin	223.3 J kg ⁻¹ K ⁻¹
Thermal conductivity at 273.2 K	
Crystal to c-axis	0.527 W cm ⁻¹ K ⁻¹
Crystal ⊥ to c-axis	0.759 W cm ⁻¹ K ⁻¹
Polycrystalline	0.628 W cm ⁻¹ K ⁻¹
Coefficient of expansion at 273 K	
Linear	19.9 × 10 ⁶
Cubical	59.8 × 10 ⁶
Single crystal (to c-axis)	28.4 × 10 ⁶
Single crystal (⊥ to c-axis)	15.8 × 10 ⁶
Expansion on melting	2.3%
Surface tension at melting point	544 mN m ⁻¹
Viscosity at melting point	1.85 mNs m ⁻²
Gas solubility in liquid tin	
Oxygen at 809 K	0.00018%
Oxygen at 1023 K	0.0049%
Hydrogen at 1273 K	0.04%
Hydrogen at 1573 K	0.036%

Table 1.6 Spectroscopic data: X-ray atomic energy levels

Designation	Energy (eV)
<i>K</i>	29200.0 ± 0.4
<i>L_I</i>	4464.7 ± 0.3
<i>L_{II}</i>	4156.1 ± 0.3
<i>L_{III}</i>	3928.8 ± 0.3
<i>M_I</i>	883.8 ± 0.3
<i>M_{II}</i>	756.4 ± 0.3
<i>M_{III}</i>	714.4 ± 0.4
<i>M_{IV}</i>	493.3 ± 0.3
<i>M_V</i>	484.8 ± 0.3
<i>N_I</i>	136.5 ± 0.4
<i>N_{II}, N_{III}</i>	88.6 ± 0.4
<i>N_{IV}, N_V</i>	23.9 ± 0.3
<i>O_I</i>	0.9 ± 0.5
<i>O_{II}, O_{III}</i>	1.1 ± 0.5

Table 1.7 Spectroscopic data: X-ray emission wavelengths

Designation	$\lambda(\text{\AA})$	Energy (keV)
$\alpha_1 KL_{II}$	0.495053	25.044
$\alpha_1 KL_{III}$	0.490599	25.2713
$\beta_2 KM_{II}$	0.435877	28.4440
$\beta_2 KM_{III}$	0.435236	28.4860
$\beta_2 KM_{II, III}$	0.425915	29.1093
$KO_{II, III}$	0.42467	29.195
$\beta_1^I KM_{IV}$	0.43184	28.710
$\beta_1^I KM_V$	0.43175	28.716
$\beta_4 KN_{IV, V}$	0.42495	29.175
$\beta_4 L_I M_{II}$	3.34335	3.7083
$\beta_3 L_I M_{III}$	3.30585	3.7500
$\gamma_{2, 3} L_I N_{II, III}$	2.8327	4.3768
$\gamma_4 L_I O_{II, III}$	2.7775	4.4638
$\eta L_{II} M_I$	3.78876	3.27234
$\beta_1 L_{II} M_{IV}$	3.38487	3.66280
$\gamma_5 L_{II} N_I$	3.08475	4.0192
$\gamma_1 L_{II} N_{IV}$	3.00115	4.13112
$\zeta L_{III} M_I$	4.07165	3.04499
$\alpha_2 L_{III} M_{IV}$	3.60891	3.43542
$\alpha_1 L_{III} M_V$	3.59994	3.44398
$\beta_1 L_{III} N_I$	3.26901	3.7926
$\beta_{2, 15} L_{III} N_{IV, V}$	3.17505	3.90486
$\beta_7 L_{III} O_I$	3.1546	3.9279
$\beta_{10} L_I M_{IV}$	3.12170	3.9716
$\beta_9 L_I M_V$	3.11513	3.9800

accompanied by a redistribution of the valence electrons, as shown by the Mössbauer isomer shifts (α -tin, $\delta=2.10 \text{ mm s}^{-1}$, β -tin, $\delta=2.65 \text{ mm s}^{-1}$), the higher value corresponding to a higher electron density in the tin $5s$ orbital for β -tin. Significantly, the redistribution of valence electron density is reflected in the reaction of the two modifications with hydrochloric acid, which with β -tin gives tin(IV) chloride pentahydrate, whereas α -tin produces tin(II) chloride dihydrate. Fusion occurs at a relatively low temperature for a metal (232°C), with a very large liquid range before a boiling point of 2270°C . Mechanically, tin is relatively weak at ambient temperatures, but tin-plating and tin-rich alloys have found extensive applications [3].

1.4 Chemical reactions

At ambient temperatures, tin is relatively unreactive and is inert to oxygen, nitrogen, hydrogen, water and ammonia. Surface oxidation does occur at elevated temperatures, resulting in significant tarnishing of the surface at 200°C . At white heat, tin is said to burn with a white flame to form tin(IV) oxide. Water vapour reacts with the tin surface at temperatures in excess of 700°C to give oxide films and hydrogen. Reagents which are oxidizing in

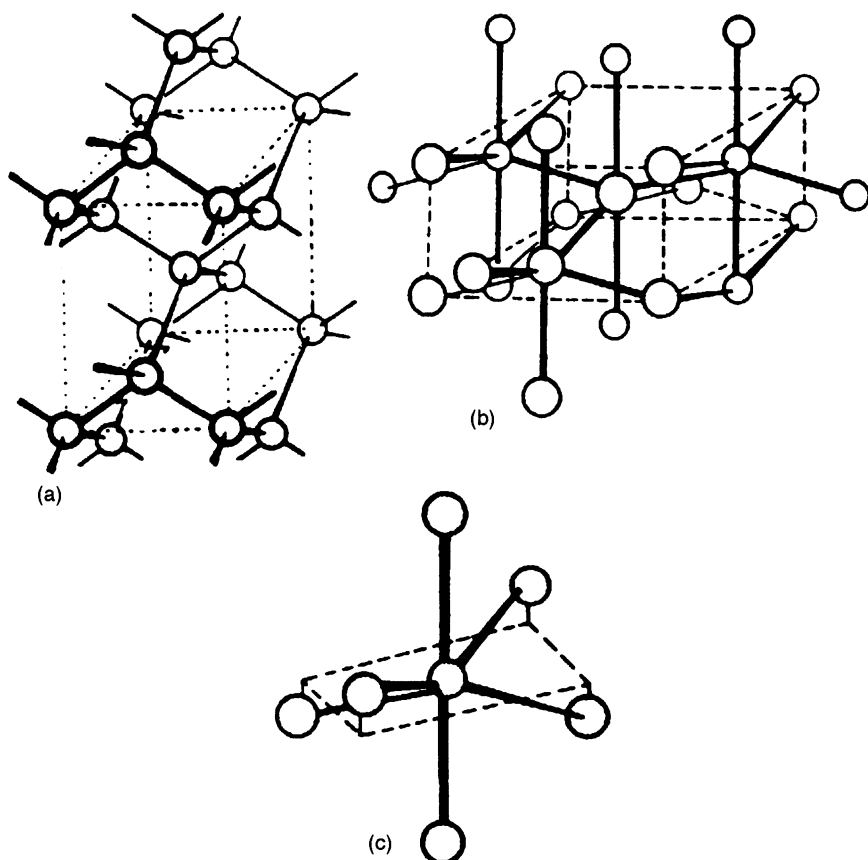


Figure 1.1 (a) The structure of α -tin, (b) the structure of β -tin and (c) the distorted tetrahedral coordination geometry of β -tin.

nature show significantly greater reactivity. Thus tin metal is attacked by chlorine and bromine to form the corresponding tin(IV) halide. Reaction with fluorine and iodine is slow below 100°C . Elemental sulphur and selenium react only on heating, when the reaction is reported to be vigorous, giving the corresponding tin(II) or tin(IV) chalcogenide, depending upon the mole ratio of reactants employed. Tin(II) telluride is formed with tellurium. Little reaction is observed with dilute hydrochloric or sulphuric acids, but dilute nitric is said to produce $\text{Sn}(\text{NO}_3)_2$ and NH_4NO_3 , although the constitution of the tin-containing product as a bivalent tin nitrate must be in doubt. Hot concentrated acids react rapidly to give tin(II) chloride, tin(II) sulphate, and 'metastannic acid', a hydrated tin(IV) oxide, respectively. The rate of reaction is dramatically enhanced in the presence of oxygen. Tin dissolves in hot aqueous alkali solutions to afford alkali metal hydroxystannates,

$M_2[Sn(OH)_6]$ ($M = Na, K$). Under near-neutral conditions, tin metal is essentially inert to corrosion, owing to the formation of a surface oxide film. However, some attack at the metal surface can occur when in contact with solutions containing chloride, sulphate or nitrate anions. Attack is much more rapid in the presence of oxidizing reagents such as persulphate. Organic acids react much more slowly, and attack by acetic or citric acids is not significant in the absence of oxygen. Bimetallic systems involving tin can also react much more rapidly.

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2 Compounds of tin: general trends

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Tin lies at the centre of the Periodic Table, and has the ability to form stable, relatively strong bonds with the majority of elements. Most of the bonds are largely σ -covalent in character, but essentially ionic bonds are formed with the heavier alkali metals and alkaline earths. Perhaps most surprising for a typical Main Group element is the rapidly developing chemistry of π -bonded polyhapto compounds exhibited by bivalent tin, an area traditionally considered to be confined to the *d*-block metals. Coupled with this tremendous versatility in bonding is the availability of a wide range of coordination geometries and lattice structural types, leading to a wealth of solid state chemistry. In this chapter is presented some of the fundamental background upon which the rich tapestry of tin chemistry is based.

2.1 Electronegativity values, ionization potentials and elemental radii

Electronegativity values, ionization potential data, and estimates of the radii of the Group 14 elements in various chemical situations are collected in Table 2.1 (see also Ref.1). The more recently devised electronegativity scales of Sanderson and Hargittai-Bliefert, which are based on analysis of infrared band intensities for MHCl_3 and MX_4 molecules and bond distance data in bivalent and tetravalent derivatives, respectively, concur with the alternating scale of Allred-Rochow, rather than the original Pauling scale. While it must be borne in mind that the absolute electronegativity varies significantly upon the particular chemical environment, it can be seen that the electronegativity varies little down the Group. The 'inert pair' effect has a much greater effect upon the electronegativity, and the values for M(II) are significantly lower than those for M(IV) , and increase in the reverse order. Values of the various radii increase with increasing atomic number, so that the covalent radius of tin is almost twice that of carbon. 'Ionic' radii are substantially smaller than the corresponding covalent radii, with the M(II) 'ionic' radii being significantly larger than the corresponding M(IV) values. The sum of the relevant van der Waals' radii is often used to assess the presence or otherwise of significant bonding interactions. These for tin with a variety of elements are collected in Table 2.2 together with typical covalent bond distances. It must be stressed that the values quoted are to be considered only as typical, and that observed bond distances can vary substantially from compound to compound.

Table 2.1 Properties of the Group 14 elements

<i>Electronegativity scales</i>					
Element	Pauling	Allred–Rochow	Sanderson	Hargittai–Bliefert	Sanderson M ^{IV} M ^{II}
C	2.5	2.5	2.5	2.6	
Si	1.8	1.7	1.7	1.9	
Ge	1.8	2.0	2.3	2.5	2.62 0.56
Sn	1.8	1.7	2.0	2.3	2.30 1.49
Pb	1.9				2.29 1.92

<i>Elemental radii (pm)</i>					
Element	Non-bonded radius	M ^{IV} covalent radius	M ^{IV} 'ionic' radius	M ^{II} 'ionic' radius	van der Waals' radius
C	125	77.2			153
Si	155	117.6	40		193
Ge	158	122.3	53	73	198
Sn	182	140.5	69	118	217
Pb		146	78	119	202

<i>Ionization potentials (eV)</i>				
Element	1st	2nd	3rd	4th
C	11.260	24.383	47.887	64.492
Si	8.151	16.345	33.492	45.141
Ge	7.899	15.934	34.22	45.71
Sn	7.344	14.632	30.502	40.734
Pb	7.416	15.032	31.937	42.32

Data taken from *Inorganic Chemistry of the Main Group Elements* (1977) The Chemical Society, Vol. 4, 145; I. Hargittai and C. Bliefert (1983) *Z. Naturforsch. B*, **38**, 1304; N.N. Greenwood and A. Earnshaw (1984) *Chemistry of the Elements*, Pergamon, Oxford, 431; C. Glidewell (1979) *Inorg. Chim. Acta*, **36**, 135; A. Bondi (1964) *J. Phys. Chem.*, **68**, 441; R.T. Sanderson (1986) *Inorg. Chem.*, **25**, 1856; and *Handbook of Chemistry and Physics* (1981) 61st edn, CRC Press, Boca Raton.

Table 2.2 Typical bond distance data together with corresponding sums of van der Waals' radii

Bond	Bond distance $r(\text{Sn-X})$ (pm)	Sum of van der Waals' $r_w(\text{Sn}) + r_w(\text{X})$ (pm)
Sn–H	215	337
Sn–F	197	352
Sn–Cl	239	397
Sn–Br	255	412
Sn–O	215	357
Sn–S	240	402
Sn–N	215	367
Sn–P	250	407
Sn–C(σ)	215	417
Sn–C(π)	274	403
Sn–Sn	275	434

Van der Waals' data from Table 2.1 and *Handbook of Chemistry and Physics* (1980–81) 61st edn, CRC Press, Boca Raton, Florida.

Whereas all the elements of the group can form compounds with four covalent bonds, the first and second ionization energies for germanium, tin and lead are similar to those of elements which readily form bivalent cations, for example (1st and 2nd ionization energies (eV) in parentheses): magnesium (7.464, 15.035); calcium (6.113, 11.871); manganese (7.435, 15.640); iron (7.870, 16.18) and cobalt (7.86, 17.06). Hence it is not surprising to find the emergence of a stable +2 oxidation state with these elements. In the case of tin, the +4 state is more stable than the +2 state, but the energy difference between the two oxidation states is quite small (electrochemical potential for the reaction $\text{Sn}^{2+} - 2\text{e}^- \rightarrow \text{Sn}^{4+}$ 0.1364 V), whereas for germanium and lead the +4 and +2 states, respectively, are dominant. Hence for tin, extensive and varied chemistries are found for both oxidation states, although the majority of bivalent tin compounds are susceptible to facile aerobic oxidation. The +3 oxidation state is generally considered unstable with respect to disproportionation. However, kinetically stable +3 species such as $\cdot\text{Sn}[\text{E}(\text{SiMe}_3)_2]_3$ (E = N, CH) have been obtained and have extremely long and perhaps indefinite lifetimes in solution.

2.2 Enthalpies of formation and bond energy data

Observed enthalpies of formation for a wide variety of compounds are collected in Table 2.3, together with calculated values for some compounds and transient species. Both bivalent and tetravalent compounds of tin are thermodynamically stable with fairly large negative enthalpies of formation. In all three series of compounds, SnX_2 , SnX_4 and Me_3SnX (X = halogen), the enthalpy of formation becomes more negative with increasing electro-

Table 2.3 Enthalpy of formation data (kJ mol^{-1})

Compound/species	$\Delta H_f(\text{c or l})$	$\Delta H_f(\text{g})$	$\Delta H_f(\text{g})$
Sn (white, tetragonal)	0.00 ^a		
Sn (grey, cubic)	2.51 ^a		
Sn		301.8	
SnO	-285.9 ^a		
SnS	-77.7 ^a		
SnF ₂		-484.9	-479.0
SnCl ₂	-349.4 ^a	-235.8	-343.6
SnBr ₂	-265.8 ^a	-121.2	-159.3
SnI ₂	-143.8 ^a	8.4	23.8
SnCl ₂ ·H ₂ O	-944.3 ^a		
Sn(C ₃ H ₃) ₂			525.4
SnO ₂	-578.1 ^a		
SnH ₄		162.6	133.3
SnCl ₄	-544.7 ^b	-471.1	-421.3
SnBr ₄	-405.9 ^a	-313.5	-127.5
SnI ₄	-214.3 ^a		
SnCl ₄ ·2py	-221.1 ^a		

Table 2.3 (*Cont'd*)

Compound/species	$\Delta H_f(c \text{ or } l)$	$\Delta H_f(g)$	$\Delta H_f(g)$
SnCl ₄ ·2isoqu	-156.3 ^a		
SnBr ₄ ·8H ₂ O	-2744.6 ^a		
Sn(SO ₄) ₂	-1644.2 ^a		
Me ₄ Sn		-19.2; -14.0	-68.6
Et ₄ Sn		-44.7	-132.9
Me ₃ SnCHCH ₃		90.7	38.5
Me ₃ SnCH ₂ Ph		88.2	55.6
Me ₃ SnPh		104.5	84.4
Me ₃ SnPr ⁱ		-46.8	-85.7
Me ₃ SnBu ⁱ		-66.9; -104.1	-66.0
Me ₃ SnH		21.7	-18.8
Me ₃ SnOH	-379.6 ^a	-316.8	-201.5
Me ₃ SnCl	-244.1 ^a	-194.0	-194.8
Me ₃ SnBr	-204.0 ^a	-140.4	-99.5
Me ₃ SnI	-130.4 ^b	-82.3	-35.9
Me ₃ SnOEt	-305.6 ^b	-263.8	-203.1
Me ₃ SnSBu ⁿ	-196.9 ^b	-155.1	
Me ₃ SnNMe ₂	-55.6 ^b	-18.0	14.2
(Me ₃ Sn) ₂ NMe	-131.7 ^b	-81.5	
(Me ₃ Sn) ₃ N	-122.1 ^a	-59.4	
Me ₃ SnSiMe ₃		-207.7	
Me ₃ SnGeMe ₃		-309.7	
Me ₃ SnSnMe ₃		-26.8; -29.8	
Me ₃ SnH ₂		87.8	
Et ₂ SnH ₂		42.6	-10.9
Me ₂ SnCl ₂		-296.8	-286.7
Me ₂ ClSnSnClMe ₂			-306.4
Ph ₃ SnEt	380		
Ph ₃ SnMe	380		
Ph ₃ SnI	380		
Ph ₃ SnSPh	543		
Ph ₃ SnSnMe ₃	359		
Sn ⁺			1008.7
Me ₃ Sn [·]			113.8; 33.6; 127.5
Me ₂ Sn ⁺			770.2; 781.7; 756.6
Me ₂ Sn—CH ₂ [·]			317.7
Me ₂ Sn=CH ₂			129.6
Me ₂ Sn			1.05
Me ₂ ClSn [·]			-100.7

^a $\Delta H_f(c)$ ^b $\Delta H_f(l)$

Data from M. Cartwright and A.A. Wolf (1976) *J. Chem. Soc., Dalton Trans.*, 829; M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding (1971) *J. Organomet. Chem.*, **29**, 195; *Selected Values of Chemical Thermodynamic Properties* (1968) Natl. Bur. Stand. Tech. Note 270-3, US Government Printing Office, Washington, DC; J.D. Cox and G. Pilcher (1970) *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York; J.C. Baldwin, M.F. Lappert, J.B. Pedley and J.S. Poland (1972) *J. Chem. Soc., Dalton Trans.*, 1943; J.M. Miller and M. Onyszczuk (1967) *J. Chem. Soc. A*, 1132; *Handbook of Chemistry and Physics* (1981) 61st edn, CRC Press, Boca Raton, Florida; M.J.S. Dewar, J.E. Friedheim and G.L. Grady (1985) *Organometallics*, **4**, 1784; M.J.S. Dewar, G.L. Grady and J.J.P. Stewart (1984) *J. Am. Chem. Soc.*, **106**, 6771; M.J.S. Dewar, G.L. Grady, D.R. Kuhn and K.M. Merz (1984) *J. Am. Chem. Soc.*, **106**, 6773; M.J.S. Dewar, G.L. Grady and D.R. Kuhn (1985) *Organometallics*, **4**, 1041; D.B. Chambers and F. Glockling (1970) *Inorg. Chim. Acta*, **4**, 150; C. Glidewell (1985) *J. Organometal. Chem.*, **294**, 173; W.J. Pietro and W.J. Henne (1982) *J. Am. Chem. Soc.*, **104**, 4329.

negativity/decreasing size. The formation of high coordination number complexes also has a dramatic stabilizing effect. Increasing the number of tin-carbon bonds in tetravalent tin compounds causes an increase in ΔH_f , and some tetraorganostannanes have positive enthalpies of formation, as do all tin hydrides. Not surprisingly, the enthalpies of formation of the transient species are usually very positive, although that of dimethylstannylene is calculated to be only $+1.05 \text{ kJ mol}^{-1}$ and that of the tin-centred radical $\text{Me}_2\text{ClSn}\cdot$ is calculated to be $-100.7 \text{ kJ mol}^{-1}$ (cf. $\text{Me}_3\text{Sn}\cdot$).

Single-bond energy data are listed in Table 2.4. Bond dissociation values vary somewhat between individual molecules, and hence only general trends in the data should be noted. The strongest bonds are formed with the more electronegative elements, oxygen and chlorine (no data appear to be available for the Sn-F bond). Strengths of bonds involving tin are, however, only

Table 2.4 Bond energy data (kJ mol^{-1})

Compound	Bond	$D(\text{R}_3\text{Sn-X})$	$E(\text{Sn-X})$
Me_4Sn	Sn-C	272; 273	201
$\text{Me}_3\text{SnBu}'$	Sn-C	246	222
Ph_3SnMe	Sn-C	259	
Ph_3SnEt	Sn-C	251	
Ph_4Sn	Sn-C	347	
Me_3SnH	Sn-H	309	
Me_3SnOH	Sn-O	460	322
Me_3SnOEt	Sn-O	351	276
Me_3SnCl	Sn-Cl	422	314
SnCl_4	Sn-Cl		315
Me_3SnBr	Sn-Br	355	255
Me_3SnI	Sn-I		188
$\text{Me}_3\text{SnSBU}''$	Sn-S		217
Ph_3SnSPh	Sn-S	288	
$\text{Me}_3\text{SnNMe}_2$	Sn-N		171
$(\text{Me}_3\text{Sn})_2\text{NMe}$	Sn-N		201
$(\text{Me}_3\text{Sn})_3\text{N}$	Sn-N		176
$\text{Me}_3\text{SnSiMe}_3$	Sn-Si	285	235
$\text{Ph}_3\text{SnSiMe}_3$	Sn-Si	280	
$\text{Me}_3\text{SnGeMe}_3$	Sn-Ge	289	225
$\text{Ph}_3\text{SnGeMe}_3$	Sn-Ge	297	
$\text{Me}_3\text{SnSnMe}_3$	Sn-Sn	234; 258	160
$\text{Ph}_3\text{SnSnPh}_3$	Sn-Sn	259	

Data from M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding (1971) *J. Organomet. Chem.*, **29**, 195; J.C. Baldwin, M.F. Lappert, J.B. Pedley and J.S. Poland (1972) *J. Chem. Soc., Dalton Trans.*, 1943; D.B. Chambers and F. Glockling (1970) *Inorg. Chim. Acta*, **4**, 150; R.A. Jackson (1979) *J. Organomet. Chem.*, **166**, 17; A.C. Baldwin, K.E. Lewis and D.M. Golden (1979) *Int. J. Chem. Kin.*, **11**, 529; T.J. Burkey, M. Majewski and D. Griller (1986) *J. Am. Chem. Soc.*, **108**, 2218; and *Selected Values of Chemical Thermodynamic Properties* (1968) Natl Bur. Stand. Tech Note 270-3, US Government Printing Office, Washington, DC.

moderately strong and, therefore, under appropriate conditions, easily cleaved.

2.3 Multiple bond formation [2]

The reluctance of the heavier elements of Group 14 to form stable compounds possessing multiple bonds is in sharp contrast to the behaviour of carbon, where $p\pi$ - $p\pi$ multiple bond formation is a major feature of its chemistry. Until recently, no stable silicon-containing analogues were known, and examples of $p\pi$ - $p\pi$ bonding were restricted to transient species which could be generated either at high temperatures or in low temperature matrices. However, routes to stable compounds have been devised, and the chemistry of compounds containing Si=Si, Si=C, Si=N and Si=P, as well as some germanium analogues, is quite extensive.

A handful of compounds exhibiting multiple bonds involving tin has been described. However, in many cases a problem arises: when is a double bond a formal double bond? Molecular geometry and shortening of bond distances compared to typical single-bond distances may be invoked as corroboration of multiple bonding. Further, albeit indirect evidence, such as stretching force constant and NMR chemical shift and one-bond coupling constant values, may be obtained from spectroscopic data. In the simplest case for which data is available, molecular SnO₂, which is formed along with Sn₂O₂ and SnO (minor product) when tin vapour is co-condensed with oxygen at 20 K in krypton or nitrogen matrices, has the same linear $D_{\infty h}$ structure as CO₂. Tin-oxygen stretching vibration force constants and Sn-O bond distances are similar for both SnO₂ and SnO (SnO₂: force constant $5.36 \times 10^2 \text{ N m}^{-1}$, Sn-O distance 181 pm; SnO: force constant $5.62 \times 10^2 \text{ N m}^{-1}$, Sn-O distance 183 pm, cf. Sn₂O₂ (containing single bonds): force constant $2.59 \times 10^2 \text{ N m}^{-1}$, Sn-O distance 205 pm), from which a bond order of 1.9 was estimated for the tin-oxygen double bond [3-6].

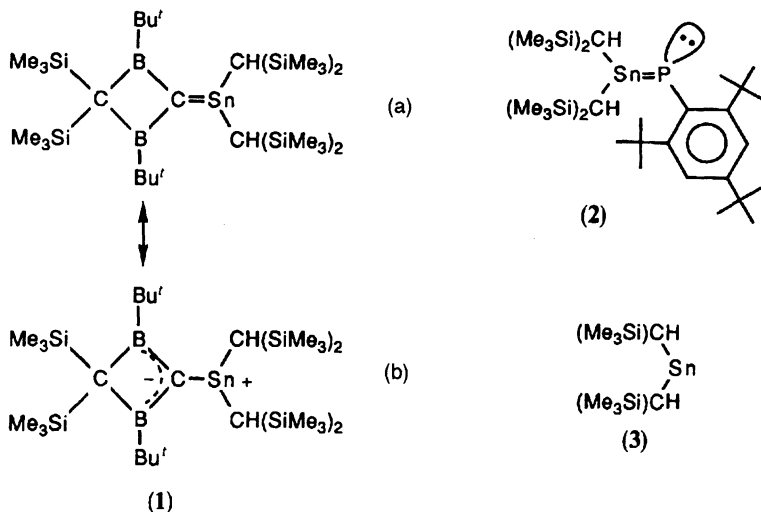
1,1-Dimethylstannaethene, Me₂Sn=CH₂, has been generated in the gas phase by proton abstraction from Me₃Sn⁺, and the Sn=C π -bond energy estimated to be 188 kJ mol⁻¹ [7]. MNDO calculations, however, cast some doubt on this figure, and predict singlet (Me₂Sn and CH₂ residues parallel) and triplet (Me₂Sn and CH₂ residues orthogonal) forms to be very similar in energy, with the triplet slightly (by 4.6 kJ mol⁻¹) more stable! In both, the tin is predicted to be pyramidal, with Sn-C bond distances of 192 pm and 199 pm for the singlet and triplet forms, respectively [8] (cf. 198.2 pm calculated [9] for H₂Sn=CH₂).

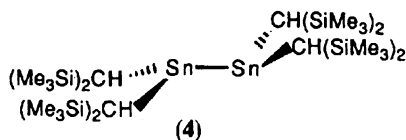
As with silicon and germanium, stable compounds containing multiple bonds involving tin (or their equivalent) have been prepared by steric crowding at the reactive double bond. Examples of three types of double bond, Sn=C, Sn=P and Sn=Sn, have been obtained. The tin atom in the

stable stannaethene (**1**) is only slightly pyramidalized, whereas the C(=Sn) carbon atom is significantly so, and the average twist angle between the SnC₂ and CB₂ residues is 61° (cf. calculated geometries for singlet and triplet Me₂Sn=CH₂). The tin–carbon double bond distance is somewhat longer (202.5 pm) than those predicted for Me₂Sn=CH₂ and H₂Sn=CH₂, but is significantly shorter than the single tin–carbon distances within the molecule (215.2 and 217.2 pm). However, although the ¹³C (142 ppm) and ¹¹⁹Sn (427.3 ppm) NMR chemical shifts are typical of tricoordinated carbon and tin atoms in the bond, the ¹¹B shift (64 ppm) is indicative of negative π charge on the boron atoms and therefore a significant contribution of the ylidic form (**1b**) to the bonding [10].

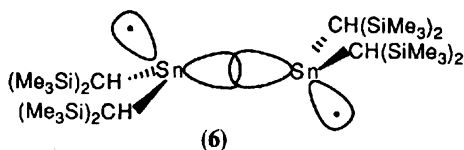
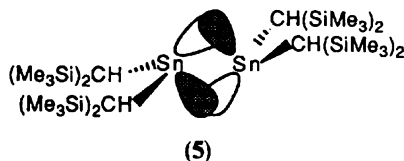
No structural data are as yet available for the stannaphosphene (**2**). Nevertheless, NMR data are again consistent with the description as a formal Sn=P double bond (δ(³¹P) 204.7 ppm, δ(¹¹⁹Sn) 658.3 ppm). Significantly, the magnitude of the one-bond ¹J(³¹P–^{117,119}Sn) coupling constant (2191, 2295 Hz) is much larger than that observed for singly bonded compounds, and expected for a high degree of π-character in the bond. The presence of a Sn=P double bond is also reflected in the reactions, which demonstrate high reactivity of the double bond towards reagents such as methanol and hydrogen chloride [11].

Two distannenes, R₂Sn=SnR₂ (R=CH(SiMe₃)₂ and C₆H₂Pr₃ⁱ-2,4,6), have been prepared, although bis[bis(trimethylsilyl)methyl]tin, Sn[CH(SiMe₃)₂]₂, has been much more widely studied. Whilst having the monomeric angular structure (**3**) in the gas phase [12], in the solid dimerization to the *trans*-bent, structure (**4**) occurs, and in solution an equilibrium between the two forms is established [13–17]. The nature of the tin–tin bond is somewhat contro-





versal, and the initial interpretation of the bonding in terms of a double 'banana' bond as in (5) has been challenged [18], albeit supported by theoretical calculations on the prototype distannene, $\text{H}_2\text{Sn}=\text{SnH}_2$ [15, 19]. A more recent theoretical description of distannene, however, favours the singly bonded biradical structure (6), in which the unpaired electrons can interact hyperconjugatively across space giving rise to a π or π -type bond, or σ -conjugatively via the Sn–Sn σ -bond [19]. This description is more consistent with the tin–tin bond distance (276.8(1) pm), which is essentially the same as that in typical tin–tin bonded tetravalent tin compounds such as $\text{Ph}_3\text{SnSnPh}_3$ (278.0(4) and 275.9(4) pm) [20] and not consistent with multiple bonding. Both dimers exhibit the very low-field ^{119}Sn chemical shifts ($\text{R}=\text{CH}(\text{SiMe}_3)_2$ [21]: solid 692 ppm, solution 725, 740 ppm; $\text{R}=\text{C}_6\text{H}_2\text{Pr}_3\text{-2,4,6}$ [22]: solution 427 ppm) usually associated with multiply bonding tin atoms. However, the dissimilarity of the two chemical shifts, together with the vastly different one-bond $^1J(^{117}\text{Sn}\text{--}^{119}\text{Sn})$ coupling constants ($\text{R}=\text{CH}(\text{SiMe}_3)_2$: $J=1340$ Hz; $\text{R}=\text{C}_6\text{H}_2\text{Pr}_3\text{-2,4,6}$: $J=2930$ Hz; cf. $\text{Me}_3\text{SnSnMe}_3$: $J=4211$ Hz [23]) and the differing solution behaviour ([tetrakis(tri-2,4,6isopropyl)phenyl]distannene retains its structural integrity in solution), suggests that the tin–tin bonding in the two distannenes is different. That in bis{bis[bis(trimethylsilyl)methyl]tin} is very weak with a very small enthalpy of dissociation (53.5 kJ mol^{-1}), and the NMR coupling constant data would be consistent with either (5) or (6), in which tin 5s contributions to the bonding would be small. The bonding in [tetrakis(tri-2,4,6isopropyl)phenyl]distannene is obviously much stronger and may involve a more formal double bond.



2.4 Structure and bonding in bivalent compounds [24–26]

2.4.1 General considerations

Application of simple VSEPR (valence shell electron pair repulsion) theory predicts an angular geometry for bivalent tin compounds, and this is indeed observed for the tin(II) halides in the gas phase [27] or isolated in a low temperature matrix [28] and for other derivatives where the steric requirements of the ligands precludes increase in coordination number at tin. The chemistry of simple monomeric bivalent tin species, SnX_2 ($\text{X}=\text{H}$, halogen, Me), usually referred to as stannylenes (IUPAC nomenclature stannanediyls), is of considerable interest as carbene analogues [29, 30]. Electronically, stannylenes behave quite differently to carbenes, which invariably exhibit a triplet (3B_1) ground state with the singlet (1A_1) state to higher energy. Like the analogous silylenes and germylenes, a singlet ground state has been calculated for the prototype stannylene [31], SnH_2 , and dimethylstannylene [32] SnMe_2 , and stannylenes behave as singlet species [33, 34]. Some structural data are collected in Table 2.5. Particularly diagnostic of the singlet electronic state is a low X-Sn-X bond angle of *c.* 90–100°. This is calculated to be

Table 2.5 Structural data for stannylene molecules

Molecule	M–X (pm)	X–M–X (°)	Ref.
SnH_2 (1A_1)	(175.6)	(92.7)	1, 2 ^a
(3B_1)	(170.7)	(118.2)	
	(177)	(93)	
SnF_2		94(5)	3
SnCl_2	234.7(7)	99(1)	4
SnBr_2	255(2)	95 ^b	5
SnMe_2 (1A_1)	(203)	(99.1)	6, 7 ^a
	(270)	(96)	
$\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$	222(2)	97(2)	2
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$	209.6(1); 208.8(6)	104.7(2)	8
$\text{Sn}(\text{OC}_6\text{H}_5\text{MeBu}_3)_2$	199.5(4); 202.2(4)	88.8(2)	9
$\text{Sn}(\text{SC}_6\text{H}_5\text{Bu}_3-2, 4, 6)_2$	243.5(1)	85.4(1)	10

^aAlso calculated values.

^bAssumed values.

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significantly higher in the triplet first excited state for SnH_2 . In addition, the Sn-H bond distance is reduced in the excited triplet state, which would appear to indicate a greater p -character for the bond in the ground state.

Bivalent tin compounds wherever possible adopt structures in which the metal achieves coordination numbers higher than two, either by complexation, chelation or by bridging. Examples of the coordination geometries found are illustrated in Table 2.6. The basic unit is usually recognizable as a

Table 2.6 Examples of coordination geometries exhibited by bivalent tin compounds

Coordination number	Coordination geometry	Examples	Ref.
2	Angular	$\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$	1
		$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$	2
		$\text{Sn}(\text{OC}_6\text{H}_2\text{Me-4-Bu}_2\text{-2,6})_2$	3
		$\text{Sn}(\text{OC}^t\text{Bu})_2$	4
		$\text{Sn}(\text{SC}_6\text{H}_2\text{Bu}_3\text{-2,4,6})_2$	5
3	Trigonal planar	$(\text{OC})_3\text{Cr}\cdot\text{Sn}[\text{CH}(\text{SiMe}_3)_2]$	6
3	Pyramidal	SnS	7
		Orthorhombic SnSe	8
		SnSO_4	9
		SnHPO_4	10
		$[\text{Sn}(\text{EPh})]_3$ ($\text{E} = \text{S}, \text{Se}$)	11
		$[\text{Sn}(\text{O}_2\text{CH})]_3$	12
4	Square pyramidal	SnO	13
		$[\text{Sn}_3\text{F}_{10}]^4$	14
		(Phthalocyaninato) Sn	15
4	ψ -Trigonal bipyramidal	SnFCl	16
		$[\text{SnCl}_4]$	17
		$\text{Sn}(\text{O}_2\text{CH})_2$	18
		$\text{Sn}(\text{OCMeCHCPhO})_2$	19
		$\text{Sn}_6\text{O}_4(\text{OMe})_4$	20
		$\text{Sn}(\text{S}_2\text{COMe})_2$	21
		$\text{Sn}[\text{C}(\text{PMe}_2)_3]_2$	22
5	Square pyramidal	$[\text{Tris}(\text{pyrazolyl})\text{borato}]\text{Sn}$	23
		$[\text{Sn}_2\text{O}(\text{O}_2\text{CCF}_3)_4\cdot\text{O}(\text{OCCF}_3)_2]$	24
		(Sn^{II} sites)	
6	Octahedral	Cubic SnSe	25
		SnTe	25, 26
6	Pentagonal bipyramidal	$[\text{Sn}_2\text{O}(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-}o)_4\cdot(\text{thf})_2]$	27
		(Sn^{II} sites)	
6	Irregular	$\{(\text{C}_5\text{H}_5)\text{Co}[\text{P}(\text{OEt})_2\text{O}]_3\}_2\text{Sn}$	28
		$\text{Sn}_2(\text{edta})\cdot 2\text{H}_2\text{O}$ (Sn^{I} site)	29
7	Irregular	$\text{Sn}_2(\text{edta})\cdot 2\text{H}_2\text{O}$ (Sn^{II} site)	29
9	Trifacially capped trigonal prismatic	SnX_2 ($\text{X} = \text{Cl}, \text{Br}$)	30, 31
		$\text{Sn}(\text{NCS})_2$	32
		$\text{Sn}(\text{SbF}_6)_2(\text{AsF}_3)_2$	33

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trigonal pyramid (7), but additional bonds or contacts are often present, leading to distorted pseudo-trigonal bipyramidal (8), square-based pyramidal (9), octahedral (10), distorted octahedral (11) or facially capped trigonal prismatic (12) coordination geometries. The most common



(7)



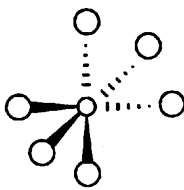
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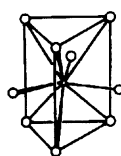
(9)



(10)



(11)



(12)

geometries are the three-coordinated trigonal pyramid and the four-coordinated pseudotrigonal bipyramid and square-based pyramid. The bond angles at tin in the trigonal pyramidal geometry are usually *c.* 90°, indicative of essentially p^3 hybridization for tin (thus placing the non-bonding electron pair in the 5s orbital). Distortions from ideal geometry are frequently encountered, and a distinction between the two four-coordinate geometries is sometimes semantic. Coordination numbers higher than four are relatively rare, and in some cases, such as the PbCl_2 -type structure exhibited by tin(II) chloride and bromide, the apparent coordination number does not reflect the number of actual bonding contacts. Indeed, in that case the stereochemistry is probably better regarded as distorted octahedral, with the basic trigonal pyramidal $[\text{SnX}_3]$ unit being supplemented by three additional longer secondary bonds in the three *trans* octahedral positions.

For the majority of compounds, and probably all with bonds to light atoms such as fluorine, oxygen and nitrogen, the tin lone pair is stereochemically active. This is usually diagnosed by the presence of an apparent vacancy in the primary coordination sphere, together with the consequent structural distortions, and also by the ability to function as a two-electron donor ligand. The only crystallographically corroborated example [35] of a complex involving coordination of the tin(II) lone pair to a Main Group Lewis acid is the complex $(\text{SnNBu}')_4 \cdot 2\text{AlCl}_3$, although the complexes $(\text{C}_5\text{H}_5)_2\text{Sn}-\text{AlX}_3$ are also proposed [36] to contain a formal Sn-Al bond. The analogous adduct with boron trifluoride is not a true stannylene complex, but rather has a complex structure with no tin-boron bonding [37]. In contrast, many complexes are known in which a tin(II) species functions as a donor to transition metal Lewis acids, and several examples are illustrated in Figure 2.1 [38–48]. The bonding between the transition metal and tin in these complexes is $\sigma + \pi$ in character, with synergistic $p\pi-d\pi$ retrodonative bonding supplementing the σ -bond. Complex formation appears to have little effect on the geometry at tin in stannylene complexes. The $[\text{C}_2\text{SnCr}]$ fragment in the $(\text{OC})_5\text{Cr} \leftarrow \text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ is coplanar [44], but that in the related $(\text{OC})_5\text{Cr} \leftarrow \text{SnBu}'_2(\text{py})$ complex is not so, due to the coordination of the pyridine nitrogen into the vacant *p*-orbital on tin [43]. In lattices in which the tin(II) enjoys near or exact octahedral coordination, the non-bonding electron pair is no longer stereochemically active, but rather is delocalized into conduction band levels.

2.4.2 Tin(II) halides and halide complexes

In the solid state, the tin(II) halides form variants of close-packed lattices with distortions arising because of the metal non-bonding pair of electrons. The $[\text{SnF}_3]$ trigonal pyramid is the basic unit of both the orthorhombic and monoclinic modifications of tin(II) fluoride. However, strong fluorine bridging results in pseudo-trigonal bipyramidal geometry at tin for the

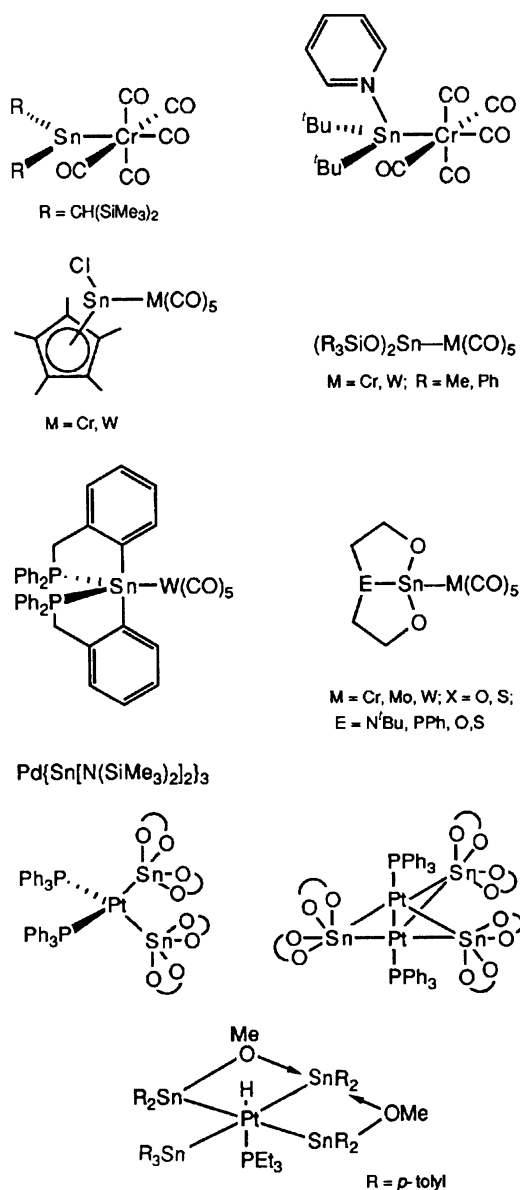


Figure 2.1 Examples of stannylene-transition metal complexes.

former and highly distorted octahedral geometry for the latter [49, 50]. Anhydrous tin(II) chloride and bromide exhibit the prototype PbCl_2 -type lattice (12) [51–53] in which the tin atom is surrounded by nine halogen atoms from three different layers, six at the apices of a trigonal prism and three in

facially capping positions. The coordination is, however, far from regular, and the metal forms three short bonds (the typical $[\text{SnX}_3]$ structural unit). The remaining halogen atoms are at much longer distances, some of which cannot represent bonding interactions. Crystals of tin(II) iodide possess a unique layer lattice, with the metal atoms occupying two different sites. Two-thirds occupy sites based on the PbCl_2 -type lattice, while the remainder are in PdCl_2 -type chains, which interlock with the PbCl_2 -type part of the structure to give almost perfect octahedral coordination [54].

A similar range of coordination geometries is also observed for halide complexes and complex anions. Although many complexes of stoichiometries $\text{MX}_2 \cdot \text{L}$ and $\text{MX}_2 \cdot 2\text{L}$ have been synthesized, the structures of only a few are known. The basic unit of the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and the thiourea complex of tin(II) chloride is again the pyramidal $[\text{SnCl}_2 \cdot \text{L}]$ ($\text{L} = \text{H}_2\text{O}$, $\text{S} = \text{C}(\text{NH}_2)_2$). However, in both adducts these units are tightly bound into three-dimensional structures by hydrogen bonding and/or chlorine and sulphur bridging [55–57]. In contrast, the structure of the 1,4-dioxan complex consists of an angular $[\text{SnCl}_2]$ unit linked by dioxan ligands to form polymeric chains with pseudo-trigonal bipyramidal geometry for tin [58]. In both the 1,10-phenanthroline and 2,2'-bipyridine complexes of tin(II) chloride, the nitrogen donor ligand chelates the tin atom with two longer and weaker contacts to chlorine resulting in the formation of chain structures [59]. The structures of the tin(II) bromide hydrates $2\text{SnBr}_2 \cdot \text{H}_2\text{O}$, $3\text{SnBr}_2 \cdot \text{H}_2\text{O}$ and $6\text{SnBr}_2 \cdot 5\text{H}_2\text{O}$ are all based on the trigonal prismatic geometry (12), in which the tin is surrounded by a trigonal prism of six bromine atoms, and further bromines, water molecules or vacancies at the facially capping sites [60].

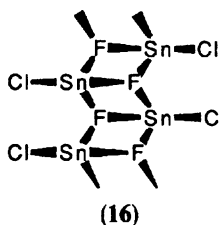
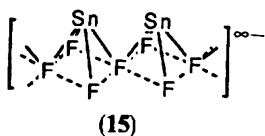
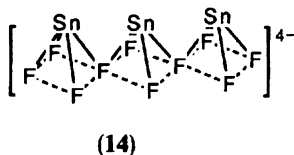
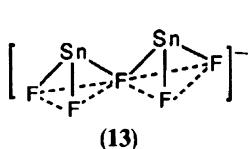
The particular structure adopted by a halogenostannate(II) salt is very dependent on the cation and halogen. Several examples of pyramidal $[\text{SnX}_3]^-$ anions have been characterized, although most involve additional longer contacts. Crystals of $[\text{NH}_4][\text{SnF}_3]$ contain essentially discrete $[\text{SnF}_3]^-$ anions [61, 62]. Discrete isolated $[\text{SnCl}_3]^-$ anions occur [63, 64] in $[\text{Co}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}][\text{SnCl}_3]$ and $[\text{Co}(\text{en})_3][\text{SnCl}_3]\text{Cl}_2$. No interaction occurs between the two anions in the latter complex, whereas the closely related compound, $[\text{Co}(\text{NH}_3)_6][\text{SnCl}_4]\text{Cl}$, contains $[\text{SnCl}_4]^{2-}$ anions of the pseudo-trigonal bipyramidal geometry [64]. An intermediate situation is present in the structure of $[\text{NH}_4]_2[\text{SnCl}_3]\text{Cl} \cdot \text{H}_2\text{O}$, where significant interaction between the chloride and trichlorostannate ions occurs. However, neighbouring $[\text{SnCl}_3 \cdots \text{Cl}]$ units are also connected by two longer $\text{Sn} \cdots \text{Cl}$ bridges forming a chain structure completing a severely distorted octahedral environment at tin [65]. A similar distorted octahedral coordination with three short and three much longer metal-halogen distances is found [61, 62] in $[\text{NH}_4][\text{SnF}_3]$, and the low temperature form [66] of CsSnCl_3 . The caesium trihalogenostannates undergo phase transitions to modifications with the cubic perovskite lattice in which the tin has ideal cubic coordination [67–71]. Ideal octahedral coordination is also found in the perovskite methylammo-

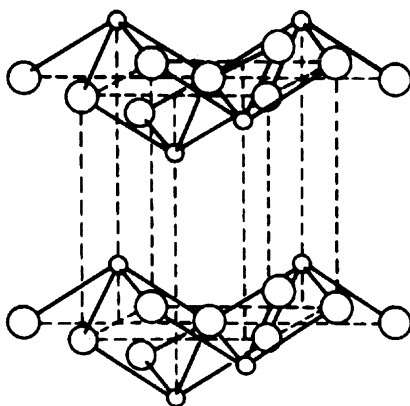
nium salts, $[\text{MeNH}_3][\text{SnBr}_x\text{I}_{3-x}]$ ($x=0$ to 3) and $[\text{MeNH}_3][\text{Sn}_{1-n}\text{Pb}_n\text{X}_3]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) [72], and CsSnI_3 [73]. In these, the tin(II) lone pair is no longer stereochemically active, and populates the lattice conduction bands, giving rise to intense colour and electrical conductivity.

The strong tendency to form Sn–F–Sn bridges observed in SnF_2 is also a prominent and dominating factor in the structural chemistry of other fluorotin(II) compounds. Only the three-coordinated pyramidal and four-coordinated pseudo-trigonal bipyramidal and square-pyramidal geometries are found. Amongst the known fluorostannate salts, the $[\text{NH}_4][\text{SnF}_3]$ salt (see above) appears to be exceptional in not exhibiting fluorine bridging. The $[\text{Sn}_2\text{F}_5]^-$ anion comprises two corner-sharing pyramids as in (13), although a fourth fluorine is located at a distance of only 253 pm from tin, and hence the structure may be regarded as containing infinite $[\text{Sn}_2\text{F}_5]_\infty^-$ anions [74]. The $[\text{Sn}_3\text{F}_{10}]^{4-}$ anion consists of three edge-sharing square pyramidal $[\text{SnF}_4]$ units as in (14) [75]. Illustrative of the profound effect on structure that the cation can have are those [76] of $[\text{NH}_4][\text{SnF}_3]$ and $\text{K}[\text{SnF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$. Whereas the former comprises isolated $[\text{SnF}_3]^-$ anions, the latter forms infinite chains of edge-sharing $[\text{SnF}_4]$ square pyramids (15), i.e. a $[\text{SnF}_3]_\infty^-$ polyanion. Cationic fluorotin(II) networks such as those found in $\text{Sn}_2\text{F}_3\text{Cl}$ [77], $\text{Sn}_3\text{F}_5\text{Br}$ [78], $\text{Sn}_2\text{F}_3\text{I}$ [79] and $[\text{Sn}_3\text{F}_9][\text{BF}_4]$ [80] have typical pyramidal $[\text{SnF}_3]$ or distorted square pyramidal $[\text{SnF}_4]$ coordination at tin with halide or tetrafluoroborate anions occupying large holes in the networks. The simple mixed tin(II) fluoride chloride [81], SnFCl , and isothiocyanate [82], $\text{SnF}(\text{NCS})$, both have a ribbon-like structure (16) propagated by four-membered $[\text{Sn}_2\text{F}_2]$ rings, with pseudo-trigonal bipyramidal tin.

2.4.3 Chalcogenide derivatives

Similar trends are observed with the chalcogenide derivatives. Tetragonal tin(II) oxide forms the layer lattice (17) with square pyramidal coordination





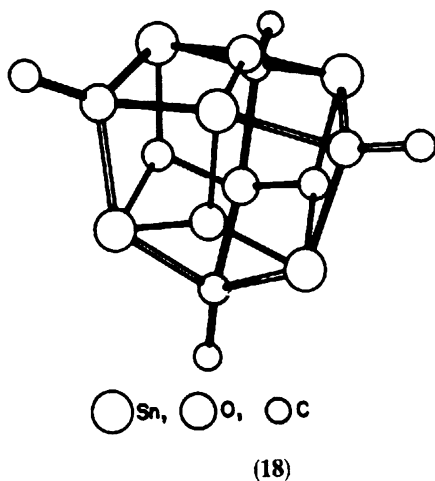
(17)

and equal tin–oxygen distances [83]. Tin(II) sulphide has a structure with parallel zigzag –Sn–S–Sn–S–Sn–S– chains, which are connected by short inter-chain $\text{Sn} \cdots \text{S}$ contacts, resulting in a basic pyramidal $[\text{SnS}_3]$ structural unit. Tin(II) selenide exhibits one phase which is isomorphous with SnS and a second cubic phase with the NaCl lattice, which is also adopted by tin(II) telluride [84–89].

Hydrolysis of tin(II) salts yields oxotin ions of several different types depending upon the conditions, particularly pH, some of which have been isolated and characterized. Structurally, they exhibit the same basic features. Thus, the sodium salts, $\text{Na}_2[\text{Sn}_2(\text{O}(\text{OH})_4)]$ and $\text{Na}_4[\text{Sn}_4(\text{O}(\text{OH})_{10})]$, contain the $[\text{Sn}(\text{OH})_3]^-$ and oxo-bridged $[(\text{HO})_2\text{SnOSn}(\text{OH})_2]^{2-}$ anions, respectively [90], while the barium salt, $\text{Ba}[\text{SnO}(\text{OH})]_2$, contains the one-dimensional $[\text{SnO}(\text{OH})]_\infty^-$ polyanion [91]. All three anions exhibit typical pyramidal coordination at tin. The discrete $[\text{Sn}_3\text{O}(\text{OH})_2]^{2-}$ cation, found in basic tin(II) sulphate, $[\text{Sn}_3\text{O}(\text{OH})_2]\text{SO}_4$, contains one tin in pyramidal coordination with two in distorted square-pyramidal four-coordination [92, 93]. Unlike polymeric anhydrous tin(II) oxide, the monohydrate $3\text{SnO} \cdot \text{H}_2\text{O}$, which can be isolated from neutral solutions, contains adamantane-type $[\text{Sn}_6\text{O}_8]$ clusters [94], very similar to those (18) found in $[\text{Sn}_6\text{O}_4(\text{OMe})_4]$ (from the controlled hydrolysis of tin(II) methoxide [95]), but again the local geometry at tin is distorted pseudo-trigonal bipyramidal.

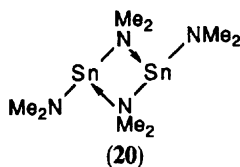
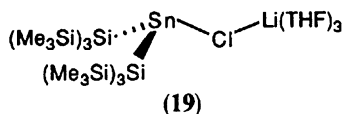
2.4.4 Molecular compounds containing bonds to elements of Groups 14, 15 and 16, and related derivatives

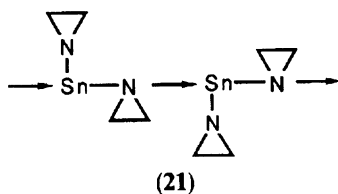
Simple σ -bonded bivalent dialkyl- or diaryltin compounds of the type R_2Sn are not stable. Rather, attempts to generate such compounds always results in the formation of isomeric metal–metal bonded cyclic oligomers, $(\text{R}_2\text{Sn})_n$, containing tetravalent tin atoms [96–100]. Predictably, this facile polymeriza-



tion process may be precluded by increasing the steric bulk of the organic groups attached to tin, as in $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ which is monomeric in the gas phase and in solution but dimeric in the solid [12–17] (section 2.3). The steric bulk of the ligand is, however, no guarantee of two-coordination, and the tin atom in the very sterically crowded bis(silyl)tin(II) derivative, $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}(\mu\text{-Cl})\text{Li}(\text{thf})_3$, is rendered three-coordinate (19) by the bridging chlorine atom. The Si–Sn–Si bond angle is nevertheless opened [101] to $114.2(4)^\circ$.

Monomeric amide, alkoxide and thiolate derivatives of bivalent tin are also only obtained with very sterically demanding ligands which preclude the possibility of bridging. Thus, the bis(trimethylsilyl)amide [102], $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$; the bis(alkoxide) [103], $\text{Sn}[\text{O}(\text{CMe}_3)_2]_2$; bis(aryloxide) [104], $\text{Sn}(\text{OC}_6\text{H}_2\text{Me-4-Bu}'_2\text{-2,6})_2$; and bis(arenethiolate) [105], $\text{Sn}(\text{SC}_6\text{H}_2\text{Me-4-Bu}'_2\text{-2,6})_2$ are all two-coordinated with an angular V-shaped geometry. Otherwise, for smaller ligands, association takes place via nitrogen, oxygen/or sulphur bridging to give dimers, trimers, or polymers depending upon the steric requirements of the particular ligand, with either pyramidal or distorted pseudo-trigonal bipyramidal geometry at tin. Thus, bis(dimethyl-amido)tin(II) exists as the dimer (20) [106], whereas a polymeric structure such as (21) has been proposed for bis(aziridinyl)tin(II) [107]. Crystals of the cyclic tin(II) amide, $[\text{SnN}(\text{Bu}')\text{SiMe}_2\text{N}(\text{Bu}')]$, comprise both monomeric and dimeric units [108]. Similarly, bis(*tert*-butoxy)tin(II) [109], bis(triphenyl-





siloxo)tin(II) [110] and 5-*tert*-butyl-5-aza-2,8-dithia-1-stanna(II)bicyclo-[3.3.0]^{1,5}octane [110], $[\text{Sn}(\text{SC}_2\text{H}_4)_2\text{NBu}^t]_2$, are dimeric, while tin(II) bis(2,6-diisopropylbenzenethiolates) are trimeric [111], and small alkoxides, $\text{Sn}(\text{OR})_2$ ($\text{R}=\text{Me}, \text{Et}$) are polymeric [112, 113]. A relatively large number of tin–nitrogen cage structures have been characterized [114], and typical members are illustrated in Figure 2.2. Both bis(di-*tert*-butylphosphino)tin(II), $\text{Sn}(\text{P}^t\text{Bu})_2$ and bis(*tert*-butylthio)tin(II), $\text{Sn}(\text{S}^t\text{Bu})_2$, are dimeric in solution [115], but their solid-state structures are not yet known. The complex thiolato- and selenatostannate(II) anions $[\text{Sn}(\text{EPh})_3]^-$ ($\text{E}=\text{S}, \text{Se}$) [116] have pyramidal three-coordination. The analogous lithium phosphino-stannate(II), $(\text{Bu}_2\text{P})\text{Sn}(\mu\text{-Bu}_2\text{P})_2\text{Li}\cdot\text{thf}$ is similar, but two of the three phosphorus atoms chelate the lithium [117].

When the ligand incorporates additional donor sites, coordination saturation at tin can be achieved either intramolecularly or intermolecularly, resulting in the formation, respectively, of discrete monomers or polymers. Thus, $\text{Sn}[\text{N}(\text{SiMe}_3)_2][\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2]$ [118], $\text{SnCl}[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2]$ [118], and $\text{Sn}[\text{CH}(\text{PPh}_2)_2][(\text{PPh}_2)_2\text{CH}]$ [119–121] are monomeric and pyramidal, whilst $\text{Sn}[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2]_2$ [118], $\text{Sn}(\text{S}_2\text{COME})_2$ [122], *N,N'*-ethylenebis(acetylideneimino) tin(II) [123], the tin(II) derivatives of 1,3-diones and related compounds [124–126], and the tetraphosphane complex, $\text{Sn}[\text{C}(\text{PMe}_2)_3]_2$ [121, 127], are all monomeric with distorted pseudo-trigonal bipyramidal geometry. Tin(II) carboxylates [128–134], sulphates [135–137] and phosphates [138–143] on the other hand, are usually polymeric in nature. Nevertheless, in spite of the large changes in gross structure, typical three- and four-coordinated geometries about the tin atom are found, and the anionic groups function as bridging ligands.

2.5 Structural behaviour of tetravalent tin compounds [25, 26]

Tetrahedral four-coordination is only observed for tin in R_4Sn ($\text{R}=\text{organic group}$) compounds and $\text{R}_n\text{SnX}_{4-n}$ derivatives which are either sterically crowded or in which the ligand is weakly electronegative and a poor donor, and tin strives to achieve coordination numbers greater than four wherever possible. The most common higher coordination numbers are five and six, although examples of seven and eight are also known. Representative exam-

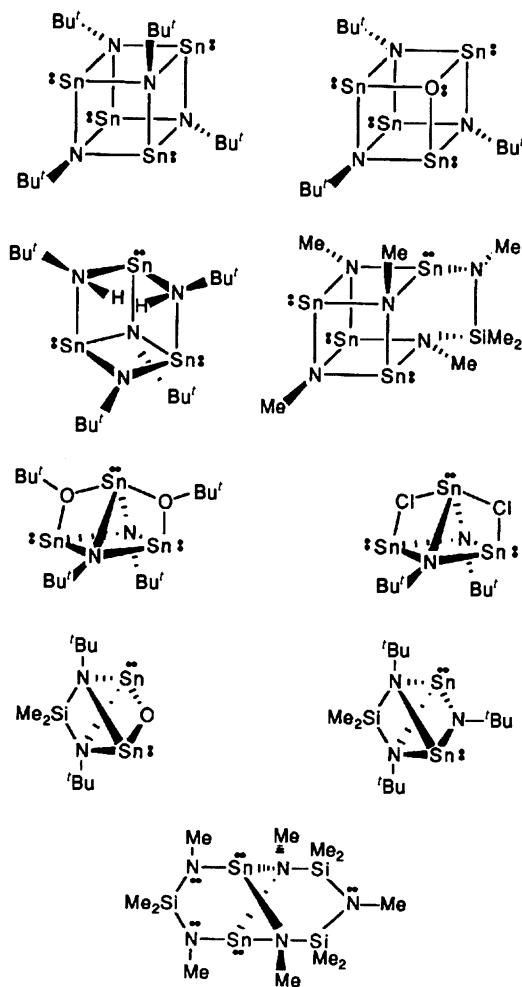


Figure 2.2 Examples of tin(II)-nitrogen compounds.

ples are shown in Table 2.7. Of the two possible five-coordinated geometries, trigonal bipyramidal and square-based pyramidal, the former predominates.

2.5.1 Hydrides and tetraorganostannanes

Stannane, SnH_4 , organotin(IV) hydrides, $(\text{SnR}_n\text{H}_{4-n})$ where $n=1$ to 3; $\text{R}=\text{alkyl}$), and most compounds with four tin-carbon bonds are tetrahedral at tin, although minor distortions can arise due to crystal packing effects [25]. Bonds to electronegative organic ligands are generally longer and weaker, and hence more susceptible to cleavage. For example, the $\text{Sn}-\text{C}$ bond

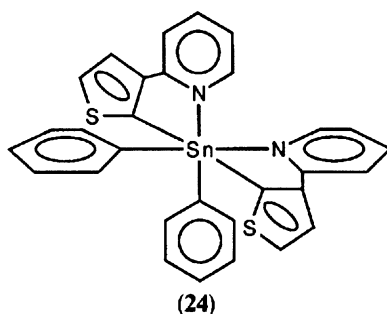
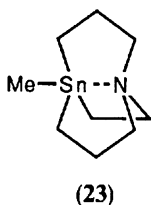
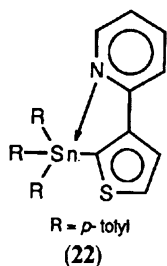
Table 2.7 Examples of coordination geometries exhibited by tetravalent tin compounds

Coordination number	Coordination geometry	Examples	Ref.
3	Trigonal planar	$[\text{SnE}_3]^{2-}$ (E = Se, Te)	1
4	Tetrahedral	Me_4Sn	2
		$(\text{CF}_3)_4\text{Sn}$	2
		Ph_4Sn	3
		$\text{Ph}_3\text{SnCH}_2\text{I}$	4
		$[(\text{Me}_3\text{Si})_3\text{C}]\text{Me}_2\text{SnF}$	5
		$(\text{PhMe}_2\text{CCH}_2)_3\text{SnCl}$	6
		$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{SnBr}$	7
		$\text{Ph}_3\text{SnSnPh}_3$	8
		$\text{Ph}_3\text{SnMn}(\text{CO})_5$	9
		K_4SnO_4	10
5	Trigonal bipyramidal	Me_3SnF	11
		$\text{Me}_3\text{SnCl}\cdot\text{py}$	12
		$\text{Me}_3\text{SnO}_2\cdot\text{CMe}$	13
		$\text{Me}_3\text{SnONPh}\cdot\text{CO}\cdot\text{Ph}$	14
		$[3-(2\text{-py})-2\text{-thienyl}](p\text{-tol})_3\text{Sn}$	15
		$\text{Ph}_3\text{SnNO}_3\cdot\text{OEPPh}_3$ (E = P, As)	16
		$[(\text{C}_6\text{H}_4\text{OS})_2\text{SnCl}]$	17
		$[\text{SnCl}_5]^-$	18
5	Square pyramidal	$[(\text{MeC}_6\text{H}_3\text{S}_2)_2\text{SnX}]$ (X = Cl, Br)	17, 19
		$(\text{PhCH}_2)_3\text{Sn}(2\text{-SC}_3\text{H}_4\text{NO})$	20
6	Octahedral	SnO_2	21
		MgSnO_4	22
		CaSnO_3	23
		Me_2SnF_2	24
		$\text{Me}_2\text{Sn}(\text{acac})_2$	25
		$[3-(2\text{-py})-2\text{-thienyl}]_2\text{Ph}_2\text{Sn}$	26
		$[\text{SnX}_6]^{2-}$ (X = F, Cl, Br, I)	18, 27, 28
6	Skew trapezoidal	$\text{Me}_2\text{Sn}(\text{NO}_3)_2$	30
		$\text{Me}_2\text{Sn}(\text{ONMe}\cdot\text{CO}\cdot\text{Me})_2$	31
		$\text{Me}_2\text{Sn}(\text{trop})_2$	32
		$\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	33
7	Pentagonal bipyramidal	$\text{Me}_2\text{Sn}(\text{NCS})_2(\text{ter})$	34
		$[\text{Me}_2\text{Sn}(\text{O}_2\text{CMe})_3]^-$	35
		$\text{MeSn}(\text{NO}_3)_3$	36
		$\text{MeSn}(\text{S}_2\text{CNEt}_2)_3$	37
8	Dodecahedral	$\text{Sn}(\text{NO}_3)_4$	38
		$\text{Sn}(\text{O}_2\text{CMe})_4$	39
8	Square anti-prismatic	Bis(phthalocyaninato)tin	40

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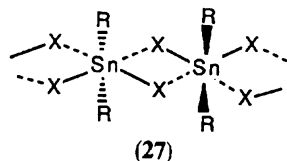
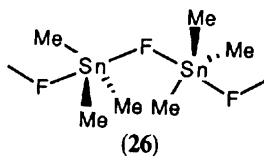
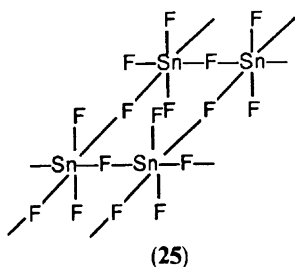
distances in $\text{Sn}(\text{CF}_3)_4$ are lengthened by 6 pm compared with those in SnMe_4 [144]. However, the tin atoms in compounds containing four tin-carbon bonds appear to be reluctant to form higher coordination numbers. Although the complex $\text{Me}_3\text{SnCF}_3 \cdot \text{P}(\text{NMe}_2)_3$ has been reported [145], tetraorganostannanes, R_4Sn , do not in general form donor-acceptor complexes with Lewis bases. Two five-coordinated examples, (22) [146] and (23) [147] and one six-coordinated example (24) [148] with four tin-carbon bonds, all involving intramolecular $\text{N} \rightarrow \text{Sn}$ coordination, have been characterized.



2.5.2 Halides and halide complexes

Tin(IV) halides, SnX_4 , and organotin(IV) halides ($\text{SnR}_n\text{X}_{4-n}$ where $n = 1$ to 3 ; $\text{R} = \text{alkyl, alkenyl, aryl}$) are tetrahedral in the vapour and liquid [25], but in the solid they exhibit a preponderance for the formation of halogen-bridged lattices. The vapour-phase data for the tetrahedral halides warrant little comment, although it is notable that the metal-halogen distance increases while the metal-carbon bond decreases in the series $\text{SnMe}_n\text{X}_{4-n}$ as the halogen content of the molecule increases, consistent with a redistribution of p character to the more electronegative ligands.

As noted for bivalent tin, fluorotin(IV) compounds exhibit a strong tendency for the formation of strong Sn-F-Sn bridges in the solid. Thus, in contrast to the heavier tin(IV) halides which are tetrahedral, tin(IV) fluoride, SnF_4 , forms a very strongly bridged, two-dimensional sheet polymer with octahedrally coordinated tin (**25**) [149]. Dimethyltin difluoride [150] (and almost certainly methyltin trifluoride [151]) has a similar sheet structure in which the non-bridging fluorine atoms are replaced by methyl groups. Fluorine bridging in trimethyltin fluoride results in a one-dimensional chain polymer with a planar $[\text{Me}_3\text{Sn}]$ moiety and trigonal bipyramidal coordination at tin (**26**) [152]. Consistent with their structures, these materials are infusible and insoluble. Other organotin fluorides are similar, and only when the organic groups are very large, as in $(\text{Me}_3\text{Si})_3\text{CSnMe}_2\text{F}$, $(\text{Me}_3\text{Si})_3\text{CSnPh}_2\text{F}$ and $(\text{PhMe}_2\text{Si})_3\text{CSnMe}_2\text{F}$ [153], does steric hindrance preclude association. Bridging by other halogens is much weaker. A loosely associated one-dimensional chain structure similar to that of Me_3SnF is formed by trimethyltin chloride at 135 K [154], whereas crystals of Ph_3SnCl [155], Ph_3SnBr [156], $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{SnCl}$ [157], $[\eta\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2]_2(p\text{-tolyl})\text{SnBr}$ [158], and $(\text{Me}_3\text{SiCH}_2)_3\text{SnI}$ [159] contain discrete, isolated molecules. The distortion away from tetrahedral geometry in tricyclohexyltin chloride suggests some intermediate state [160]. Association into one-dimensional chains occurs for dialkyltin dihalides when the alkyl group is small, and two types of structure have been characterized. In dimethyltin dichloride [161] and diethyltin dichloride and dibromide [162], the chains are formed by the two covalently bonded halogen atoms on each tin bridged to two different tin atoms in the chain as in (**27**), whereas in diethyltin diiodide [162] and bis(chloromethyl)tin



dichloride [163] the two halogen atoms essentially chelate the next tin atom in the chain as in (28). In both, the geometry at tin is highly distorted, and is best regarded as intermediate between tetrahedral and octahedral. No intermolecular interaction appears to be present in bis(biphenyl-2)tin dichloride [164] or bis(ferrocenyl)tin dichloride [165]. Diphenyltin dichloride [166, 167] and methylphenyltin dichloride [168] form loose tetrameric fragments which can be regarded as intermediate between the associated and unassociated extremes.

Higher coordination numbers at tin in organotin halides can also arise by intramolecular coordination of a donor atom remote in the organic ligand. Examples are shown in Figure 2.3 [169–175]. When two nitrogen atoms are present on the organic group, ionization of halide from tin can occur, as in (29) [176]. The methylphenyltin homologues (Figure 2.3) contain chiral tin atoms and exhibit high optical stability, since the intramolecular coordination blocks the pathways for stereoisomerization. However, dynamic processes do occur which have been examined by variable-temperature NMR, and involve Sn–N bond dissociation and inversion at the then uncoordinated nitrogen atom [175, 177]. Analogous processes have been observed in the cationic species (29) [176].

The tin(IV) halides, MX_4 , and organotin halides, $\text{SnR}_{4-n}\text{X}_n$, are good Lewis acids and acceptors of halide and neutral donor molecules. Lewis acidity in these halides increases in the order $\text{I} < \text{Br} < \text{Cl} < \text{F}$ and $1 < 2 < 3 < 4$. The pyridine adduct of trimethyltin chloride, $\text{Me}_3\text{SnCl} \cdot \text{C}_5\text{H}_5\text{N}$, was the first

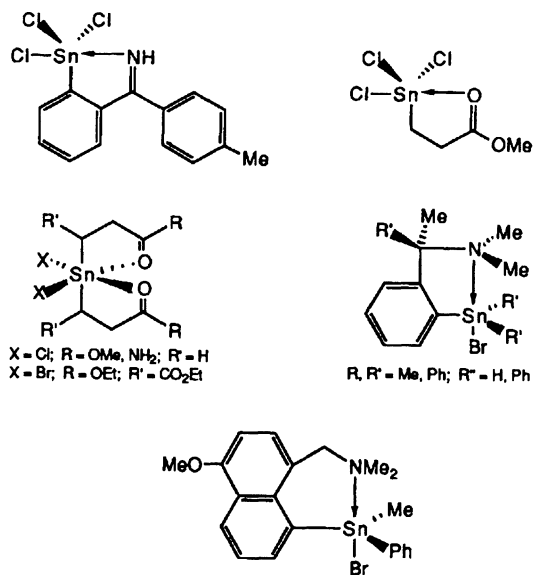
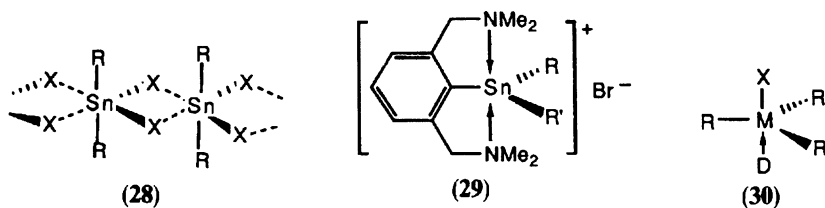


Figure 2.3 Examples of intramolecularly coordinated organotin halides.



authenticated example of a tin compound with coordination number greater than four [178]. Coordination saturation appears to be reached in the trigonal bipyramidal arrangement (30) with a planar or near-planar $[\text{SnR}_3]$ moiety for the monohalides, but the dihalides, trihalides and tetrahalides can form 1:2 adducts with an octahedral geometry as well as 1:1 adducts with the trigonal bipyramidal geometry. In the latter, the organic groups always occupy equatorial sites.

Typical examples of five- and six-coordinated complexes and complex anions are listed in Table 2.8. The 1:1 adduct of dimethyltin dichloride and diphenylcyclopropenone is unusual, and comprises a chlorine-bridged dimer with distorted octahedral geometry for tin (31) [179], rather than the usual trigonal bipyramidal geometry found in other 1:1 complexes such as $\text{Ph}_2\text{SnCl}_2 \cdot \text{benzthiazole}$ [180], i.e. the small steric requirements of the donor permit close approach of bridging chloride. Similar bridged anions such as (32) have also been isolated [181, 182]. Two types of behaviour are observed with terdentate ligands. In some isolated cases, seven-coordinated adducts with a distorted pentagonal geometry such as (33) are formed [183, 184], but

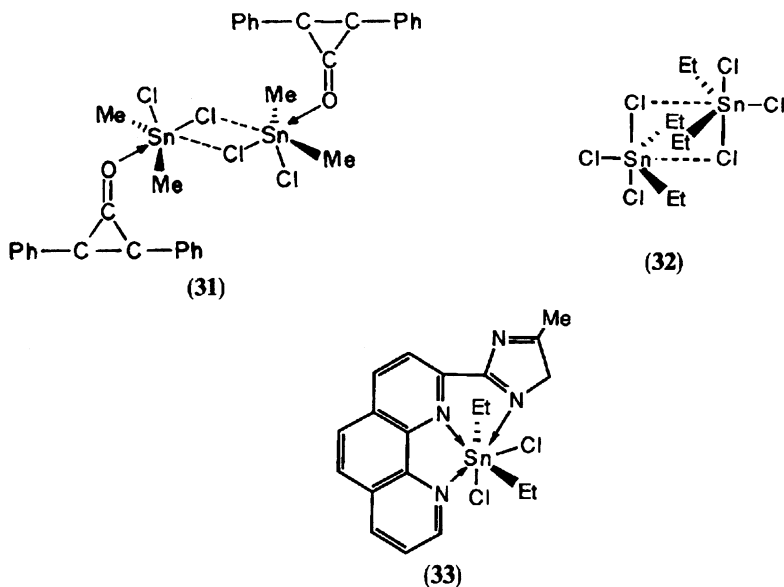


Table 2.8 Examples of five- and six-coordinate tin(IV) halide complexes and complex anions

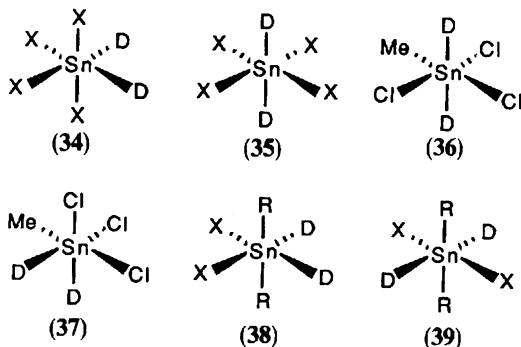
Complex	Ref.	Complex	Ref.
[SnF ₆] ²⁻	1, 2	[MeSnCl ₄] ⁻	16
SnF ₄ ·bipy	3	[Me ₂ SnCl ₃] ⁻	17
[SnCl ₅] ⁻	4–6	[Me ₂ SnCl ₃] ₂ ²⁻	18
[SnCl ₆] ²⁻	6–9	[Me ₆ Sn ₃ Cl ₈] ²⁻	19
[SnCl ₅ (OPCl ₃)]	10	[Me ₂ SnCl ₄] ²⁻	16
SnCl ₄ ·2CH ₃ CN	11	[Me ₃ SnCl ₂] ⁻	17
SnCl ₄ ·2dmsO	12	Me ₂ SnCl·Ph ₃ PCHCOMe	20
[Sn ₂ Cl ₁₀] ²⁻	6	Me ₂ SnCl ₂ ·2dmsO	21, 22
[SnBr ₆] ²⁻	13	Ph ₂ SnCl ₂ ·bipy	23
SnI ₄ ·2dpso	14	MeSnCl ₃ ·2py	24
[SnCl(S ₂ C ₆ H ₃ Me)]	15	MeSnI ₃ ·2dpso	25

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terpyridine promotes the displacement of halide from tin and the formation of ionic complexes such as [Me₂Sn(ter)Cl]⁺[Me₂SnCl₃]⁻ containing six-coordinated cations and five-coordinated anions [185]. Ionization of halide takes place more readily with bromine and iodine. Thus, whereas hexamethylphosphoric triamide forms a neutral, trigonal bipyramidal adduct with trimethyltin chloride, the ionic complex [Me₃Sn(hmpt)₂]⁺[Me₃SnBr₂]⁻ is formed with trimethyltin bromide [186].

Various stereochemical permutations are observed for octahedral tin

complexes. Adducts of tin(IV) chloride and bromide exhibit the *cis* geometry (34) [187–195], although some examples of the *trans* geometry (35) are known [196–200]. The preference for the *cis* configuration has been rationalized by simple ligand field theory whereby the splitting between the d_{z^2} and $d_{x^2-y^2}$ orbitals would be minimized [201]. When the steric bulk of the two donor atoms is too great, the *trans* geometry is adopted. The structures adopted by the complexes of organotin trihalides and diorganotin dihalides also vary with the particular donor ligands. The two donors are *trans* in the 2:1 pyridine and HMPT complexes of methyltin trichloride as in (36), but the analogous DMF complex adopts the *cis* structure (37) [202, 203]. The two organic groups in $R_2SnX_2 \cdot 2L$ complexes are invariably *trans*, although the isolation of both *cis* and *trans* isomers for $(4-ClC_6H_4)_2SnCl_2 \cdot (4,4'-dimethyl-2,2'-bipyridyl)$ demonstrates the small differences in energy between the two forms [204]. The two halide and two donor molecules can adopt either configuration (38) or (39), depending upon the nature of the substituents [205–214].



2.5.3 Chalcogenides and chalcogenide complex ions

Tin(IV) oxide crystallizes in the rutile lattice (Figure 2.4) in which the tin atoms enjoy almost perfect octahedral coordination with only a small tetragonal distortion [215]. Tin(IV) sulphide and selenide both crystallize with the hexagonal CdI_2 layer lattice also with six-coordinated tin [216], and many polytypes have been characterized [217–219].

The structures adopted by stannates are profoundly different to those of silicates and germanates, in spite of the similarity in stoichiometries. Tin is in general six-coordinated in a regular or slightly distorted octahedral fashion by oxygen atoms, although four- and five-coordination do occur. Octahedral oxygen coordination about tin is present in all the hydroxystannates(IV), $M[Sn(OH)_6]$ ($M = 2Na, 2K, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd$) [220–228]. The structures of the metal hexahydroxystannates and of the crystalline metal stannates, $MSnO_3$, obtained by calcination of the hexahy-

droxystannates above 500–600 °C are dependent upon the radius of the M^{2+} cation. The former are cubic with a NaCl-type lattice below 126 pm and hexagonal above this size, whilst the latter have an ilmenite-type structure when the M^{2+} radius is less than 109 pm and a perovskite type above 126 pm [229]. Potassium orthostannate, K_4SnO_4 , contains isolated $[SnO_4]$ tetrahedra [230–232], but other materials of the stoichiometry M_2SnO_4 ($M = Mg, Ca, Sr, Ba, Mn, Co, Cd, Zn$) are not true orthostannates, and contain $[SnO_6]$ octahedra which share common edges to give chain or layer structures [233–238]. Octahedrally coordinated tin is also present in the ‘distannates’, $M_2Sn_2O_7$ ($M = \text{lanthanide, Bi}$) [239–241], and most ‘metastannates’, $MnSnO_3$ ($M = 2Li, 2Tl, Mg, Ca, Sr, Ba, Mn, Cd, Pb$) [242–248]. The potassium and rubidium metastannates, however, have unusual square-pyramidal five-coordination for tin, and the solid contains infinite $[SnO_3]_{\infty}^{--}$ polyanions as shown in Figure 2.5 [249, 250].

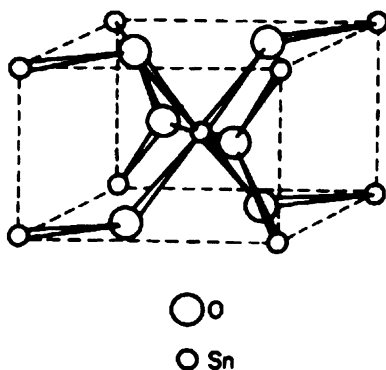


Figure 2.4 The unit cell of tin(IV) oxide.

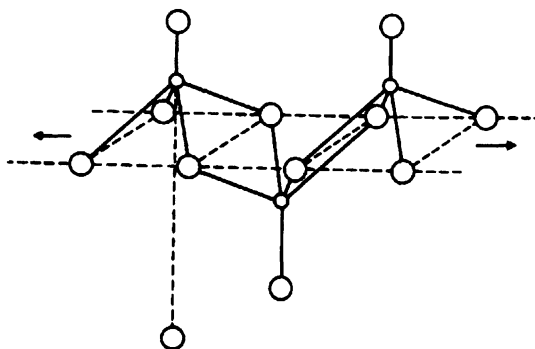
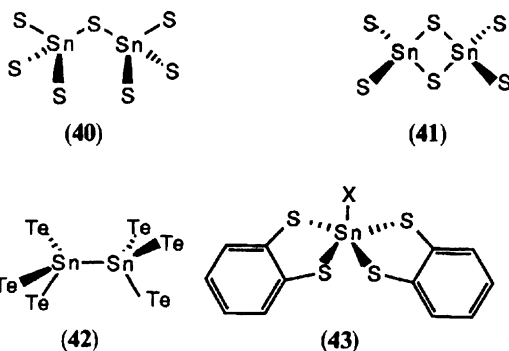


Figure 2.5 The structure of the infinite $[SnO_3]_{\infty}^{--}$ polyanions in M_2SnO_3 ($M = K, Rb$).

The structures of the heavier chalcogen analogues of the stannates are largely based upon the tetrahedral $[\text{SnX}_4]$ unit. All three isolated orthostannate anions $[\text{SnX}_4]^{4-}$ ($\text{X}=\text{S}, \text{Se}, \text{Te}$) have been characterized [251–260]. The trigonal planar $[\text{SnX}_3]^{2-}$ anions are also known [259]. Three types of binuclear anion are known. $[\text{Sn}_2\text{S}_7]^{6-}$ [252, 261, 262] and $[\text{Sn}_2\text{S}_6]^{4-}$ [263, 264] are formed by vertex- (40) and edge-sharing (41), respectively, of two $[\text{SnS}_4]$ tetrahedra, but the tellurium derivative, $[\text{Sn}_2\text{Te}_6]^{6-}$, contains the Sn–Sn bonded arrangement (42) with a staggered conformation [265–267]. The metathiostannates, $\text{K}_2\text{SnS}_3 \cdot 2\text{H}_2\text{O}$ [268] form infinite $[\text{SnS}_3]^{2-}$ chains. Coordination numbers greater than four are less frequent than for the stannates. The tin atom has a distorted octahedral geometry in the lanthanide thiostannates, Ln_2SnS_5 [269, 270], Fe_2SnS_4 [271] and Mn_2SnS_4 [272].

Complex anions derived from chelating oxo and thio ligands exhibit five- or six-coordination depending upon the nature of the chelating ligand. The two bis(toluene-3,4-dithiolato)halogenostannate anions, $[(\text{C}_7\text{H}_6\text{S}_2)_2\text{XSn}]^-$ ($\text{X}=\text{Cl}, \text{Br}$) (43), are two of the very few authentic examples of square pyramidal five-coordination at tin, being very close to ideality along the Berry pseudorotation coordinate ($\text{X}=\text{Cl}$: 76.9%; $\text{X}=\text{Br}$: 94.2%). Replacement of one of the sulphur atoms in the chelate ring, or of the halogen by hydroxyl, causes a change in stereochemistry to trigonal bipyramidal five-coordination as in the $[(\text{C}_6\text{H}_4\text{OS})_2\text{SnCl}]^-$ anion or octahedral as in the $[(\text{CN})_2\text{C}_2\text{S}_2)_2\text{SnOH}]^-$ anion [273, 274].



2.5.4 Organotin derivatives with bonds to elements of Groups 15 and 16

As a result of the greater effective nuclear charge at tin coupled with the high donor capacity of oxygen, few organotin compounds containing bonds to oxygen remain tetrahedral at tin. Rather, association via intermolecular oxygen bridging occurs in the solid wherever possible. Only when steric hindrance precludes association does four-coordination occur in such compounds as hexaphenyl- and hexabenzoyldistannoxanes, $\text{R}_3\text{SnOSnR}_3$,

($R = \text{Ph}, \text{PhCH}_2$) [275, 276]. The former compound is expectedly bent at oxygen, but the SnOSn skeleton in the latter is surprisingly linear, a phenomenon which has been attributed to the low electronegativity of the metal coupled with the electron-donating character of the organic group [276].

Other triorganotin derivatives of oxygen ligands such as hydroxide [277, 278], alkoxides [279–281] and oximes [282] show a marked tendency to associate into one-dimensional chain polymers in which planar or near-planar $[\text{R}_3\text{Sn}]$ units are bridged by oxygen atoms as in (44). Steric crowding at tin reduces this tendency towards association, but increasing the size of the substituent at oxygen has less effect. Thus, whereas $\text{Me}_3\text{SnON}=\text{C}_6\text{H}_{11}$ has the structure (44), very similar to those of Me_3SnOH and Me_3SnOMe , as the organic group attached to tin increases in size, the association along the series $\text{R}_3\text{SnON}=\text{C}_6\text{H}_{11}$ ($R = \text{Me}, \text{Et}, \text{Pr}^i\text{Ph}$) becomes weaker and the $[\text{R}_3\text{Sn}]$ moiety becomes more pyramidal (45) until for $\text{Ph}_3\text{SnON}=\text{C}_6\text{H}_{11}$, the solid comprises isolated tetrahedral (46) molecules [283, 284]. Similarly, homologous methoxides such as tri-*n*-butyltin methoxide exist as oils where association is negligible. However, higher triorganotin hydroxides such as tri-*n*-butyltin and triphenyltin hydroxides are still associated [285, 286].

Similar polymeric chain structures involving planar bridged $[\text{R}_3\text{Sn}]$ moieties are adopted by several other types of triorganotin derivative including carboxylates, oxyacid derivatives such as sulphates, sulphonates, phosphates and nitrates, and pseudo-halides, and examples are listed in Table 2.9. Some of the chains are linear, others helical, but the most unusual, and at present unique, is the cyclic hexamer formed by triphenyltin diphenylphosphate, $\text{Ph}_3\text{SnO}_2\text{P}(\text{OPh})_2$ [287] (Figure 2.6). Observed structures of triorganotin carboxylates fall into three categories. The majority, including trimethyl-, trivinyl-, triphenyl-, and tribenzyltin carboxylates, possess the rather tightly bound one-dimensional polymeric structure (47), with the carboxylato groups strongly bridging the triorganotin residues in the

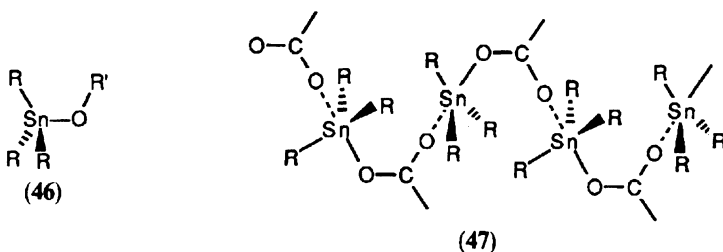
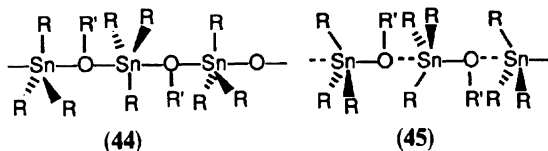
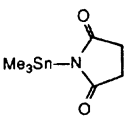
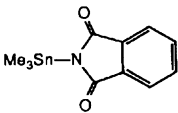
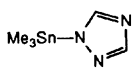
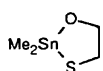


Table 2.9 Examples of triorganotin compounds exhibiting one-dimensional associated structures

Compound	Ref.	Compound	Ref.
Me ₃ SnOH	1,2	Me ₃ SnNCO·Me ₃ SnOH	23
Ph ₃ SnOH	3	Ph ₃ SnNCO	24
Me ₃ SnOMe	4	Me ₃ SnN(CH ₃)NO ₂	25
Me ₃ SnON=C ₆ H ₁₀	5	Me ₃ Sn—N·S·N:S:NSO ₂	26
Me ₃ SnO ₂ CCH ₃	6		27
Me ₃ SnO ₂ CCF ₃	6		
(Me ₃ SnO ₂ C)CH ₂	7		28
Me ₃ SnO ₂ CH ₂ NH ₂	8		
(CH ₂ =CH) ₃ SnO ₂ CCl ₃	9		29
(PhCH ₂) ₃ SnO ₂ CCH ₃	10		
Ph ₃ SnO ₂ CCH ₃	11		30
Me ₃ SnNO ₃	12		
Me ₃ SnO ₂ SCH ₃	13, 14		
Me ₃ SnO ₂ SeCH ₃	15		
Me ₃ SnO ₂ P(OH)Ph	16		
Me ₃ SnO ₂ PCl ₂	17		
Me ₃ SnO ₂ P(CH ₃) ₂	17		
Me ₃ SnN ₃	18		
Me ₃ SnN(CN) ₂	19		
Me ₃ SnN:C:NSnMe ₃	20		
Me ₃ SnNCS	21		
Ph ₃ SnNCS	22		

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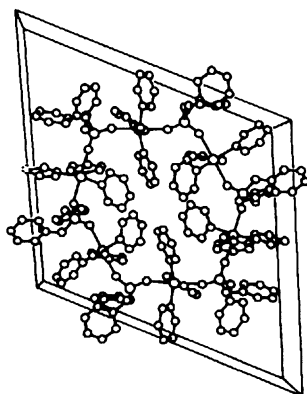
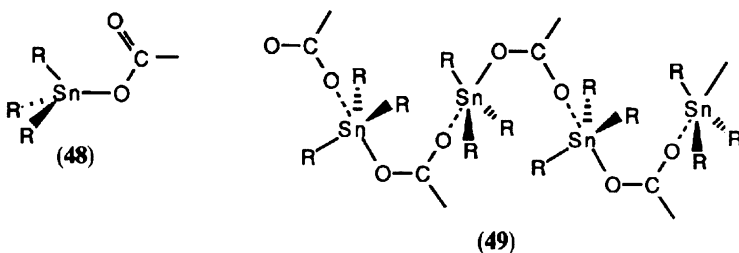


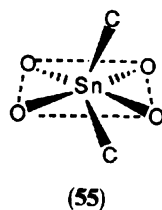
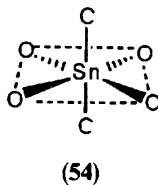
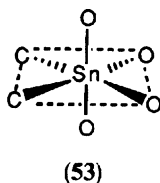
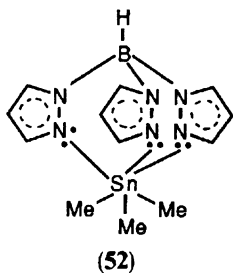
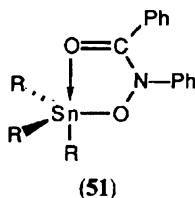
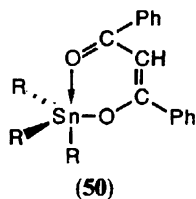
Figure 2.6 The hexameric structure of $\text{Ph}_3\text{SnO}_3\text{P(OPh)}_2$. Phenyl rings on the phosphate group have been omitted. (Redrawn by permission from Ref. 287.)

usual *syn*, *anti* fashion. Tricyclohexyltin carboxylates, although having been previously misrepresented as examples of monomeric triorganotin carboxylates with unidentate carboxylato ligands and four-coordinate tin as in (48), have a similar structure (49), although the *syn*, *anti* bridging is longer and weaker. Few examples of monomeric triorganotin carboxylates have been characterized, and these involve a very high degree of steric crowding. Except for $(\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO}_2\text{SnPh}_3)$, the chelation of the carboxylato ligand is unsymmetrical. Triphenyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate adopts a distorted trigonal bipyramidal geometry where the carboxylate group chelates via an axial and an equatorial site [288–292]. Hydrated triorganotin derivatives retain the trigonal bipyramidal geometry at tin with the water molecule occupying an equatorial site, with $[\text{R}_3\text{SnX}\cdot\text{H}_2\text{O}]$ units linked by hydrogen bonding [293, 294].



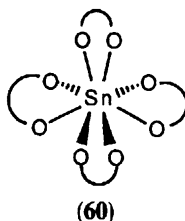
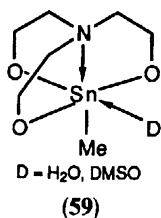
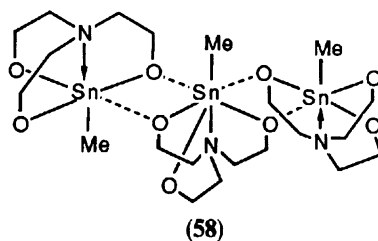
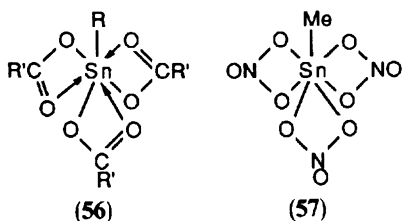
Triorganotin derivatives of strongly chelating oxygen ligands such as acetylacetonate [295] and *N*-acylhydroxylamines [296, 297] exhibit contrasting behaviour, and exhibit the *cis* trigonal bipyramidal geometry (**50**) and (**51**). [Tris(pyrazolyl)borato]-trimethyltin, [HB(pz)₃]₃SnMe₃, (**52**) is unique, being the only authenticated example amongst triorganotin compounds of six-coordination [298].

Few examples of four-coordinated organotin compounds containing two or three tin–oxygen bonds have been characterized, although it is highly likely that this geometry occurs in sterically crowded compounds such as Ph_nSn(OSiPh₃)_{4-n} (*n* = 1, 2). Di- and trialkoxides with less sterically demanding substituents appear to be associated [299]. The favoured coordination geometries for diorganotin derivatives of carboxylic acids, inorganic oxyacids and related hydroxy species are *cis* (**53**) and *trans* (**54**) octahedral, and skew-trapezoidal (**55**) (intermediate between tetrahedral four-coordination and octahedral six-coordination), although examples of seven- and eight-coordination geometries have been found. Both bridging and chelation can occur with bifunctional ligands, but *a priori* predictions concerning the solid-state structure can be unwise, as the particular structure can vary tremendously within the same class of compound. For instance, dimethyltin diacetate [300] is monomeric in the crystal, adopting the skew-trapezoidal structure with chelating acetato groups. Dimethyltin dipicolinate, on the other hand, has a polymeric structure in which both picolinate ligands chelate the tin atom via one oxygen and the nitrogen, with seven-coordination being completed by a bridging oxygen [301]. Dimethyltin derivatives of oxyacids appear to adopt bridged structures. For example, dimethyltin bis(fluoro-sulphonate), Me₂Sn(OSO₂F)₂, has a polymeric sheet structure [302], and

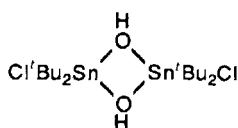


dimethyltin phosphate, $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$, adopts an infinite 'ribbon' structure [303]. The structures of a large number of diorganotin derivatives, R_2SnL_2 , of potentially chelating groups (L) are known, all of which exhibit $[\text{SnC}_2\text{O}_4]$ six-coordination with the C–Sn–C bond angle varying from the *cis* octahedral geometry (53), through varying degrees of the skew-trapezoidal structure (55) to the *trans*-octahedral geometry (54). The majority of compounds in this group possess the skew-trapezoidal geometry, intermediate between the two extremes of *cis*-octahedral, exemplified by dimethyltin bis(oxinate) [304] and $\text{Me}_2\text{Sn}(\text{ONHCOMe})_2$ [305], and *trans*-octahedral, exemplified by $\text{Me}_2\text{Sn}(\text{acac})_2$ [306]. Several factors obviously contribute to the particular geometry adopted in these compounds. However, the series of closely related compounds. $\text{Me}_2\text{Sn}(\text{ONMeCOMe})_2$ (C–Sn–C angle 145.8°) [307], $\text{Me}_2\text{Sn}(\text{ONHCOMe})_2$ (C–Sn–C angle 109.1°) [305] and $\text{Me}_2\text{Sn}(\text{ONHCOMe})_2 \cdot \text{H}_2\text{O}$ (C–Sn–C angle 156.8°) [305], illustrate the rather large effect that hydrogen bonding and crystal packing effects can have upon the stereochemistry adopted about the tin atoms.

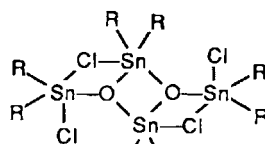
Little is known concerning the structural chemistry of monoorganotin derivatives. Infrared and colligative data support the seven-coordinate structure (56) for monoorganotin tris(carboxylates) [308], similar to that determined for methyltin trinitrate (57) [309]. Methyltin trimethoxide forms infinite $-(\text{O}-\text{Sn}-)_\infty$ chains [310]. Intramolecular N–Sn coordination occurs in methylstannatrane, $\text{MeSn}(\text{OCH}_2\text{CH}_2)_3\text{N}$, and association into trimeric units (58) results in six- and seven coordination at tin [311–314]. In donor solvents the association is broken down, and mononuclear species (59) exist in water and DMSO. Tin(IV) nitrate [315] and tin(IV) acetate [316] have an eight-coordinate dodecahedral structure (60).



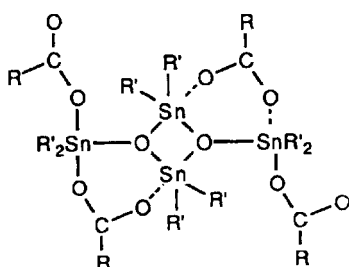
Hydrolysis of di- and monoorganotin halides or carboxylates yields a number of structural types which are formal intermediates en route to the products of exhaustive hydrolysis, the diorganotin oxides, R_2SnO , and monoorganotin oxides, $RSnO_{3/2}$, [or 'stannonic acids', $RSn(OH)O$]. Hydrolysis of di-*tert*-butyltin dihalides, $Bu_t^2SnX_2$ ($X=F, Cl, Br$), affords the dimeric halide hydroxides, $[Bu_t^2Sn(OH)X]_2$ (**61**), which are characterized by a central four-membered $[Sn_2O_2]$ ring [317]. This structural feature is a dominant feature in the structural chemistry of oxotin compounds, and its occurrence is very widespread (Table 2.10). With less bulky organic groups, the intermediate halide hydroxide is not stable, and condensation to a dimeric 1,3-dichlorodistannoxane (**62**) occurs spontaneously. Several examples of these and other similar 1,3-dicarboxylato- (**63**) and 1-chloro-3-hydroxydistannoxanes (**64**), 1, 3-dihydroxydistannoxanes (**65**) and tristannoxanes have been characterized, and exhibit 'ladder' structures composed of fused four-membered $[Sn_2O_2]$ rings [318–326]. The initial product in the hydrolysis of monoalkyltin trichlorides is the dimeric species $[RSn(OH)(OH_2)Cl_2]_2$ (**66**) [327, 328]. Two further structural types, 'ladder' (**67**) and 'drum' (**68**)



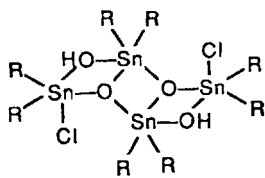
(61)



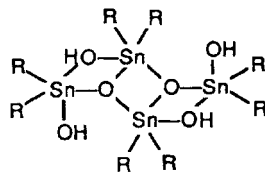
(62)



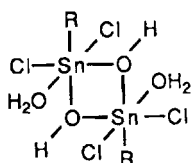
(63)



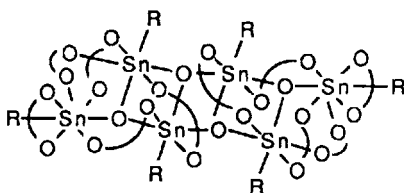
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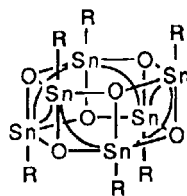
(65)



(66)



(67)



(68)

Table 2.10 Examples of compounds containing the four-membered [Sn₂O₂] ring

Compound	Structural type	Ref.
[ClMe ₂ SnOSnMe ₂ Cl] ₂	Ladder	1
[ClPh ₂ SnOSnPh ₂ Cl] ₂	Ladder	2
[ClPh ₂ SnOSnPh ₂ (OH)] ₂	Ladder	2
[(SCN)Me ₂ SnOSnMe ₂ (NCS)] ₂	Ladder	3
[(F ₃ CCO ₂)Me ₂ SnOSnMe ₂ (O ₂ CCF ₃)] ₂	Ladder	4
[(Cl ₃ CCO ₂)Bu ⁿ ₂ SnOSnBu ⁿ ₂ (O ₂ CCCl ₃)] ₂	Ladder	5
[(Me ₂ SiCH ₂) ₂ (HO)SnOSn(OH)(CH ₂ SiMe ₃) ₂] ₂	Ladder	6
[(Bu ⁿ Sn(O)O ₂ CPh) ₂ -Bu ⁿ Sn(Cl)(O ₂ CPh) ₂] ₂	Ladder	7
[(Bu ⁿ Sn(O)O ₂ CR) ₂ (Bu ⁿ Sn(O ₂ CR) ₂)] ₂ (R = Me, Ph, C ₆ H ₁₁)	Ladder	7, 8
[(MeSn(O)O ₂ CC ₆ H ₁₁) ₂ -MeSn(O ₂ CC ₆ H ₁₁) ₂] ₂	Ladder	8
[PhSn(O)O ₂ CC ₆ H ₁₁] ₆	Drum	9
[Bu ⁿ Sn(O)O ₂ CR] ₆ (R = C ₅ H ₉ , C ₆ H ₁₁ , C ₆ H ₄ NO ₂ -2)	Drum	7, 8
[(Bu ⁿ Sn(OH)O ₂ PPh ₃) ₃ O][Ph ₂ PO ₂] ₂	Cluster	10
[Bu ⁿ Sn(O)O ₂ P(C ₆ H ₁₁) ₂] ₄	Cubane drum	11
[SnCl ₃ (OH)·H ₂ O] ₂ ·4H ₂ O	Ladder	12
[SnCl ₃ (OH)·H ₂ O] ₂ ·3diox	Ladder	12, 13
[SnCl ₃ (OR)·MeOR] ₂ (R = Me, Et)	Ladder	14, 15
[SnCl ₃ (PO ₂ Cl ₂)·POCl ₃] ₂	Ladder	16
[Sn ₂ O ₂ Cl ₄ (ClO ₄) ₄] ₂	Ladder	17
[Sn ₂ (O ₂ CC ₆ H ₄ NO ₂ -2) ₄ O·thf] ₂	Cluster	18
[Bu ⁿ Sn(OH)X] ₂ (X = F, Cl, Br)	Dimer	19
[RSn(OH)(OH ₂)Cl ₂] ₂ (R = Et, Bu ⁿ)	Dimer	20, 21
[(C ₂ H ₄ OS) ₂ SnCl ₂][H][Et ₄ N]	Dimer	21
[((NC) ₂ C ₂ S ₂) ₂ SnOH] ₂ (Et ₄ N) ₂	Dimer	21
[Me ₂ Sn(O ₂ C ₂ H ₄) _n] _n	Ribbon Polymer	22
SnO	Sheet polymer	23
SnO ₂	3-D polymer	24
[Sn(OBu ⁿ) ₂] ₂	Dimer	25
Sn ₆ O ₄ (OMe) ₄	Cluster	26
[Sn ₈ O ₄](SO ₄) ₄	Cluster	27

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structures, have also been discerned in the monoorganotin system (Table 2.10), and are interconvertible in solution. Related to the 'drum' structure are two other types of cage exhibited by monobutyltin oxide phosphinates. That of $[\text{Bu}^n\text{Sn}(\text{O})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$ is characterized by a central $[\text{Sn}_4\text{O}_4]$ cube (Figure 2.7) [329], while in $[(\text{Bu}^n\text{Sn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$ a tricoordinating oxygen atom caps a trisnnoxane ring in a 'chair' conformation (Figure 2.8) [330].

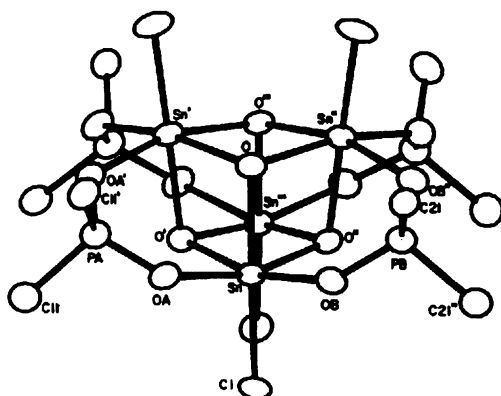


Figure 2.7 The structure of $[\text{Bu}^n\text{Sn}(\text{O})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$ illustrating the $[\text{Sn}_4\text{O}_4]$ cubane core. (Reproduced by permission from Ref. 329.)

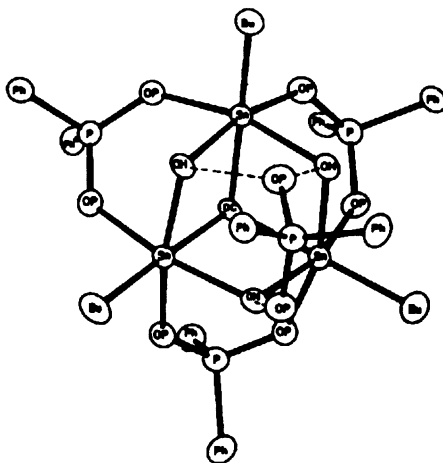
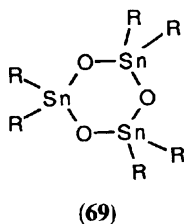
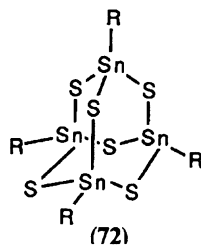
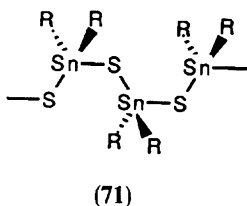
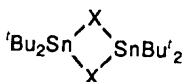


Figure 2.8 The structure of $[(\text{Bu}^n\text{Sn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$. (Reproduced by permission from Ref. 330.)

Few unequivocal structural data are available for diorganotin oxides, R_2SnO , and monoorganotin oxides, $RSnO_{3/2}$, which usually exist as insoluble and infusible amorphous solids obtained by the exhaustive hydrolysis of the corresponding organotin halides or carboxylates. From the foregoing data, it would seem highly probable that the principal structural element in these compounds is the four-membered $[Sn_2O_2]$ ring. Crystallographic data are available for only two rather esoteric cases, di-*tert*-butyl- and bis(2,6-diethylphenyl)tin oxides, which crystallize as trimeric molecules (69) with a planar six-membered $[Sn_3O_3]$ ring [331, 332], the bulky organic groups presumably precluding further association. Spectroscopic data, however, indicate a crosslinked, three-dimensional network for less sterically hindered oxides, in which the stereochemistry at tin is distorted trigonal bipyramidal with the organic groups occupying equatorial sites. Two models which have been proposed involving networks of fused [4+6]- or [4+8]-membered stannoxane rings are illustrated in Figure 2.9. The structures of the monoorganotin oxides are expected to be similar.



Associated and chelated structures are far less prevalent in compounds containing bonds to the heavier chalcogenides. Triorganotin thiolates, R_3SnSR' , are monomeric and tetrahedral [333–337], as are the tin atoms in $(Me_3SnS)_3P=S$ [338]. Weak intermolecular Sn–N interactions do, however, occur in $Ph_3SnSC_5H_4N-4$ [339], causing severe distortions of the geometry at tin towards a trigonal bipyramid. Likewise, bis(triphenyltin) sulphide [340] and selenide [341] are monomeric molecules which are bent at sulphur or selenium and contain tetrahedral tin. In contrast to the diorganotin oxides, the diorganotin chalcogenides form ring structures, most commonly a cyclic trimer with a twist-boat conformation [342]. However, with bulky



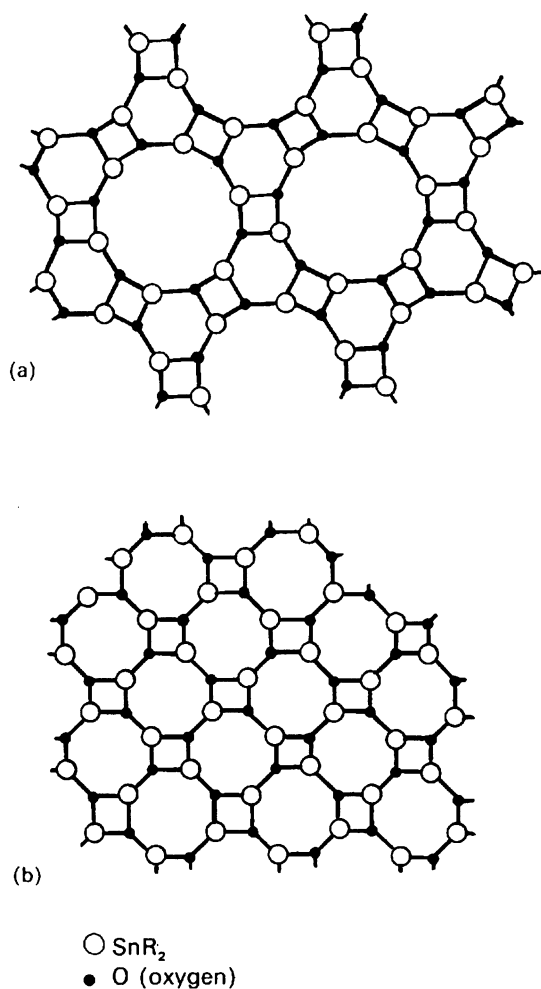


Figure 2.9 Possible solid state structures of diorganotin oxides (a) with fused [4+6] stannoxane rings or (b) with fused [4+8] stannoxane rings.

substituents, a four-membered ring may be stabilized, and di-*tert*-butyltin sulphide, selenide and telluride exist as the dimers (70) with a planar central $[\text{Sn}_2\text{X}_2]$ ($\text{X}=\text{S}, \text{Se}, \text{Te}$) ring [343]. Some diorganotin sulphides may also exist in a polymeric modification of lower solubility and higher melting point than the trimeric form, and probably have the same linear polymeric structure (71) as that characterized for diisopropyltin sulphide [344]. The monoorganotin sesquisulphides generally crystallize with the adamantane skeleton (72) [345–349].

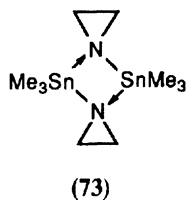
In contrast to carboxylato and other oxyanion ligands, dithio ligands such

as dithiocarbamate and dithiophosphate function as unidentate ligands in their triorganotin derivatives [350–352]. When two or fewer tin–carbon bonds are present, chelation can occur to give a skew-trapezoidal (e.g. dimethyltin bis(dithiocarbamates), $\text{Me}_2\text{Sn}(\text{S}_2\text{CNR}_2)_2$ ($\text{R} = \text{Me}, \text{Et}$) [353, 354] and diphenyltin bis(dithiophosphate), $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OEt})_2]_2$ [355]), or *trans*-octahedral structure (e.g. $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OPr}^i)_2]_2$) [356]. Methyltin tris(diethyl-dithiocarbamate) has a distorted pentagonal bipyramidal geometry, in which two dithiocarbamate groups chelate via equatorial sites while the third spans an equatorial and axial site [357]. However, the coordination in dimethyltin bis(diethylphosphinate), $\text{Me}_2\text{Sn}(\text{S}_2\text{PEt}_2)_2$, is best regarded as distorted tetrahedral since the secondary $\text{Sn} \dots \text{S}$ contacts are quite long [358].

Tetrahedral four-coordination is generally the rule for organotin derivatives of amines and phosphines, although trimethyltin aziridine is associated in the solid via N–Sn bridging and dimeric in solution (**73**) [359]. Unusually, but like the silicon and germanium analogues, $(\text{Me}_3\text{Sn})_3\text{N}$ is planar at nitrogen [360], which has been ascribed principally to electrostatic interactions [361, 362]. With phosphorus, a diverse range of ring and cage frameworks are formed, with ring sizes varying from three to six, although few structures have been determined. Examples are illustrated in Figure 2.10 [363–369].

2.6 Mixed-valence compounds

Compounds incorporating tin atoms in both valence states exhibit structures which in general endeavour to accommodate the stereochemical and bonding requirements of each, although in some cases unusual coordination geometries are found for bivalent tin. Thus, simple binary compounds such as $\text{Sn}^{\text{IV}}\text{Sn}^{\text{II}}_2\text{F}_8$ [370] and $\text{Sn}^{\text{IV}}\text{Sn}^{\text{II}}\text{S}_3$ [371, 372] have polymeric lattices with trigonal pyramidal tin(II) and octahedral tin(IV) atoms. With more sophisticated compounds such as the mixed-valence carboxylates, $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2-o)_4\text{O}\cdot\text{thf}]_2$ [373], $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}_2\text{CCF}_3)_4\text{O}]_2\cdot\text{C}_6\text{H}_6$ [374] and $[\text{Sn}^{\text{II}}_4\text{Sn}^{\text{IV}}\text{O}_2(\text{O}_2\text{CCF}_3)_6]$ [375], where the tin(IV) atoms exhibit the expected octahedral coordination, the tin(II) atoms exhibit pentagonal pyramidal or square-based pyramidal coordination polyhedra. The former represents the only example of this stereochemistry in Group 14. Similarly, in



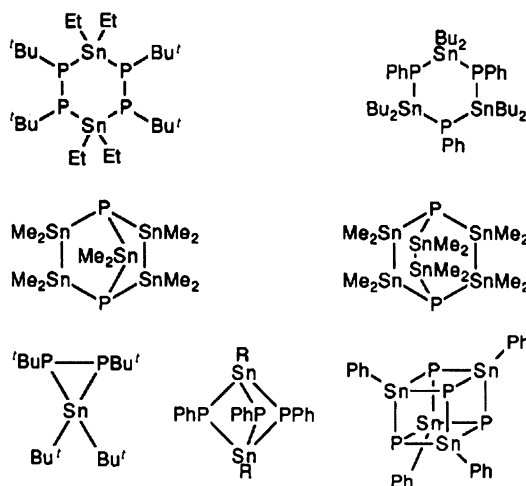
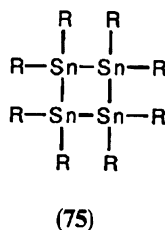
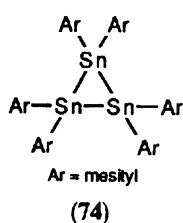


Figure 2.10 Examples of tin-phosphorus ring and cage compounds.

the triphenyltin derivatives, $\text{Sn}^{\text{IV}}(\text{C}_6\text{H}_4\text{PPh}_2\text{-}o)_3\text{Sn}^{\text{II}}\text{Cl}$ [40], $\text{Ph}_3\text{Sn}^{\text{IV}}\text{-Sn}^{\text{II}}(\text{NO}_3)$ [376] and $[\text{Ph}_3\text{Sn}^{\text{IV}}\text{-Sn}^{\text{II}}(\text{NO}_3)\cdot\text{Ph}_3\text{As}]_2$ [376], the tin(IV) atoms are tetrahedrally coordinated whereas the coordination of the tin(II) varies substantially.

2.7 Compounds with metal-metal bonds

Catenation is not extensive in tin chemistry, and chains or rings can only be obtained if substituted by organic groups. Linear chains containing up to six tin atoms and several six-membered cyclostannanes have been characterized [377–379], but smaller three- or four-membered rings such as (74) [380] and (75) [381, 382] can only be obtained with very bulky groups. Compounds containing bonds to other metals are abundant, as Chapter 7 demonstrates. The tin atoms are generally tetrahedrally coordinated, but examples with coordination numbers of five and six with bonds to both Main Group and

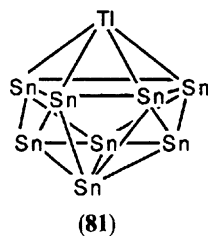
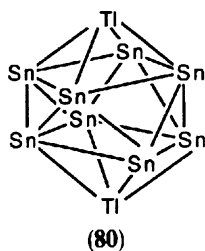
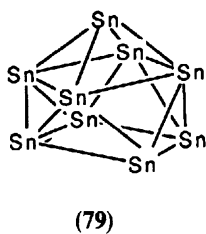
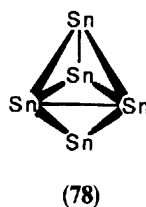
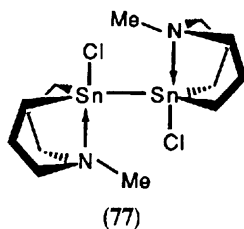
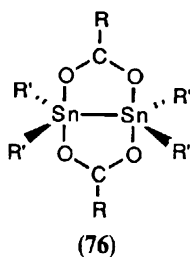


transition metals such as (76) [383], (77) [384], $(\text{acac})_2\text{Sn}[\text{CO}_2(\text{CO})_7]$ [385] and $\text{Cl}_3\text{Sn}[\text{Mo}(\text{CO})_3(\text{dth})\text{Cl}]$ [386] have also been obtained.

Complexes containing tin–metal bonds formed by the coordination of a tin(II) lone pair to a Main Group or transition metal have been described in section 2.4.1 and also in Chapter 6. More unusual are the polytin zintl anions such as $[\text{Sn}_4]^{4-}$, $[\text{Sn}_5]^{2-}$ and $[\text{Sn}_9]^{4-}$, which have tetrahedral, trigonal bipyramidal (78) and monocapped square anti-prismatic (79) structures, respectively [260, 387–391]. These species are generally not very stable and require large cations for their isolation, but appear to have significant future application. For example, thin films of AuSn alloy may be grown by immersing gold foil in a solution containing $[\text{Sn}_9]^{4-}$ [392]. Mixed zintl anions have also been characterized. The $[\text{Sn}_2\text{Bi}_2]^{2-}$ is the first heteroatomic example of the P_4 family of 20-electron tetrahedral clusters. The two anions $[\text{TlSn}_9]^{3-}$ and $[\text{TlSn}_8]^{3-}$ occur together in the same phase, and have the bicapped square anti-prismatic (80) and tricapped trigonal prismatic (81) geometries, respectively [393, 394].

2.8 Theoretical studies of reaction pathways [8, 32]

Apart from studies of the cleavage of the tin–carbon bond (Chapter 4), few studies concerning the mechanistic aspects of the reactions of tin compounds have been carried out. The alternative theoretical approach to this problem, employing even fairly simple methods such as MNDO (modified neglect of diatomic overlap) calculations, has been applied with some success, and could probably be used much more widely.



2.8.1 Hydrostannylation

The chain propagating step of the free-radical hydrostannylation of alkenes involves the reversible addition of a tin-centred radical, $R_3Sn\cdot$, to the alkene, $R'_2C=CR'_2$, to form the β -radical, $R_3SnCR'_2CR'_2\cdot$. MNDO calculations of the model reaction between the $Me_3Sn\cdot$ radical and ethene predict it to be exothermic by 67.7 kJ mol^{-1} , which is *c.* 33 kJ mol^{-1} more negative than experimental estimates. Calculated geometries and enthalpies of formation for the species participating in the reaction are shown in Figure 2.11. Of the two possible geometries for the β -radical, that in which the tin–carbon bond is parallel to the axis of the singly occupied carbon *p*-orbital (**82**) is calculated to be slightly more stable (by 10.5 kJ mol^{-1}) than the alternative rotamer (**83**). The barrier to reaction is very low (20.5 kJ mol^{-1}) in agreement with the rapid and reversible nature of the reaction, and leads to an equilibrium constant value of 5×10^4 . The structure calculated for the transition state (**84**) involves little distortion from the two reactants, with a very long nascent Sn–C bond.

2.8.2 Insertion of stannylenes into reactive bonds

Dimethylstannylene is known to undergo facile insertion into the Sn–Cl bond

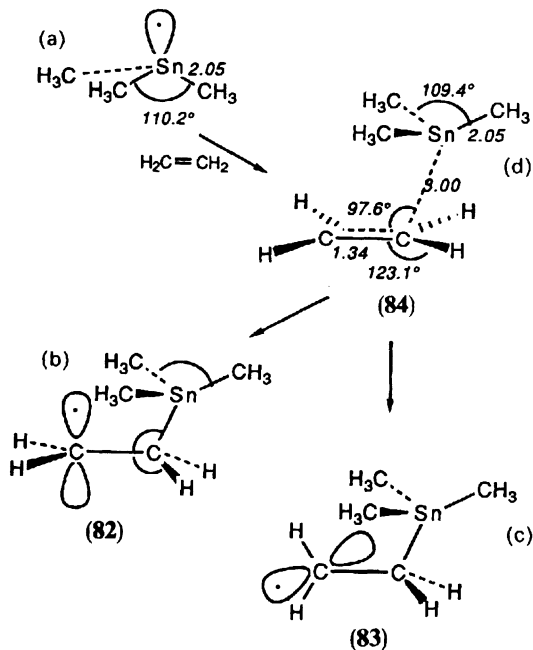
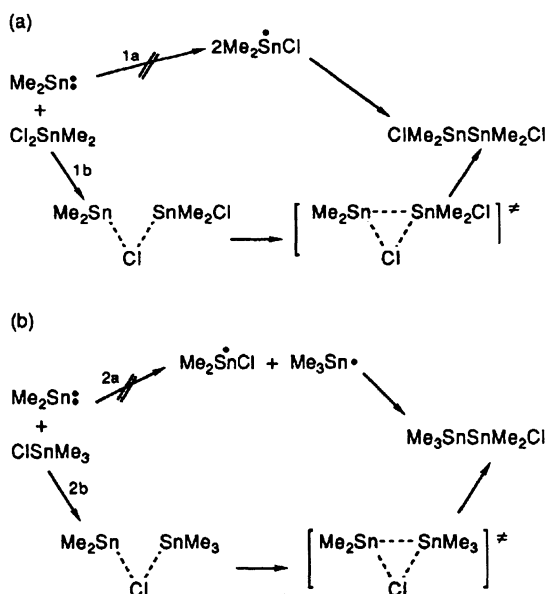


Figure 2.11 Calculated geometries for the $Me_3Sn\cdot$ radical (a), the adducts with ethene with the Sn–C bond parallel (b) or perpendicular (c) to the axis of the singly occupied atomic orbital on carbon, and the transition state (d).

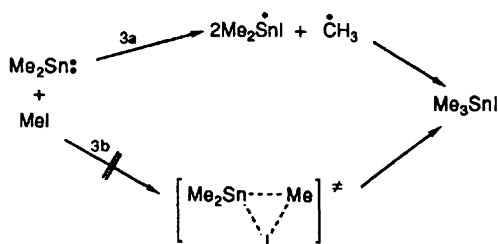
of Me_2SnCl_2 and the C–I bond of methyl iodide, but only polymerizes in the presence of Me_3SnCl . This reluctance to insert into the Sn–Cl bond of Me_3SnCl was attributed to kinetic factors ascribed to the lower positive charge on tin in Me_3SnCl . Two reaction pathways are possible for such insertion reactions, one involving a two-step process involving radicals or alternatively a direct concerted insertion. MNDO calculations predict the concerted process to occur for dimethylstannylene insertions into the Sn–Cl bonds of both Me_3SnCl and Me_2SnCl_2 via an initial adduct formed by association of the stannylene with the chlorine of the methyltin chloride, i.e. pathways 1a and 2a, rather than 1b and 2b (Scheme 2.1). In each case, the activation energy for the two-step process was significantly greater (Me_3SnCl : 59.4 kJ mol^{-1} ; Me_2SnCl_2 : 41.8 kJ mol^{-1}) than for the concerted process, and since the activation energy for reaction with Me_3SnCl is higher, the reaction rate is slower allowing polymerization to occur. In contrast, the two-step process is predicted for insertion into the C–I bond of methyl iodide, i.e. pathway 3b rather than 3a (Scheme 2.2).

2.8.3 Cycloaddition reactions of stannylenes

MNDO calculations on the cycloaddition of tin(II) bromide to butadiene, which is reported to proceed by a concerted disrotary process, predict it to

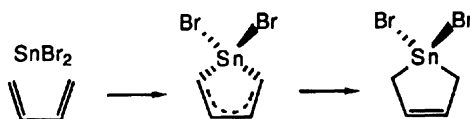


Scheme 2.1 Calculated reaction pathways for the insertion of Me_2Sn into the Sn–Cl bonds of (a) Me_3SnCl_2 and (b) Me_3SnCl .



Scheme 2.2 Calculated reaction pathways for the insertion of Me_2Sn into the C–I bond of MeI.

take place *syn* and in a synchronous manner via a symmetrical transition state (Scheme 2.3). The calculated activation energy (81.5 kJ mol^{-1}) is quite low, and is consistent with the observation that the reaction occurs at ambient temperatures.



Scheme 2.3 Calculated reaction pathways for the cycloaddition of SnBr_2 to butadiene.

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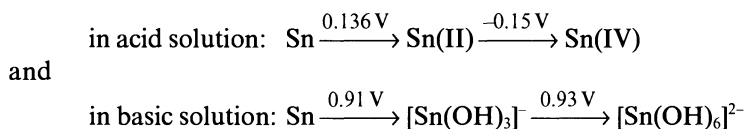
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3 The inorganic chemistry of tin

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Tin forms inorganic compounds in the +4 oxidation state by using all of its valence shell electrons in bonding, and in the +2 oxidation state in which, formally, only the *p*-electrons are used leaving a non-bonding electron pair. Many compounds in both oxidation states are known. The +4 oxidation state is the more stable state and tin(II) compounds are moderately strong reducing agents [1]. The Sn–Sn(II)–Sn(IV) potentials are:



These potentials explain why tin(IV) in acid solution can be readily reduced to tin metal and why the disproportionation of $[\text{Sn(OH)}_3]^-$ to elemental tin and $[\text{Sn(OH)}_6]^{2-}$ occurs to an appreciable extent in alkaline tin(II) solutions. The inorganic chemistry of tin in this chapter is discussed under the headings tin(II) chemistry, tin(IV) chemistry and mixed-valence tin compounds.

3.1 Tin(II) chemistry

3.1.1 Solution chemistry of tin(II) [1]

Tin(II) oxide is amphoteric and dissolves in aqueous solutions of both acids and alkalis. The predominant species present in acid solutions containing complexing anions are the pyramidal triligandstannate(II) ions, $[\text{SnX}_3]^-$ e.g. with $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{HCO}_2^-, \text{CH}_3\text{CO}_2^-$ and NCS^- . There is very little evidence for the formation of complexes with coordination greater than three. This is to be expected because the formation of $[\text{SnX}_3]^-$ from a normal tin(II) compound (SnX_2) results in the filling of the empty *p*-orbital on the tin. Since the *s*–*d* energy gap (~14 eV) in tin is much greater than the *s*–*p* gap (~7 eV), use of *d*-orbitals to increase the coordination above three is less likely. The $[\text{SnX}_3]^-$ ions can therefore be regarded as being based on a tetrahedral distribution of electron pairs around the tin with one orbital occupied by a non-bonding electron pair. The $[\text{SnF}_3]^-$ anion is the stable and predominant ion in solutions containing an excess of F^- but, when insufficient F^- is present to complex all of the tin as $[\text{SnF}_3]^-$, the polynuclear ion $[\text{Sn}_2\text{F}_3]^-$ is formed in which the preferred three-coordination for Sn(II) is preserved by a

bridging F atom. The only other Sn(II)–F species for which there is any evidence are $[\text{SnF}]^+$, $[\text{Sn}_3\text{F}_5]_n^+$ and SnF_2 . Various techniques have been used to establish the complexes present in Cl^- , Br^- and NCS^- -containing solutions, and evidence has been found for $[\text{SnX}]^+$ and SnX_2 in addition to the predominant $[\text{SnX}_3]^-$ ions. Nitrogen is the donor atom in the NCS complexes. Mixed halide complexes of the type $[\text{SnF}_2\text{Cl}]^-$ are also known. The main species in tin(II)-monocarboxylic acid solutions are the tricarboxylato-stannate(II) ions, $[\text{Sn}(\text{RCO}_2)_3]^-$, but there is also evidence for the formation of less stable complexes, for example, $[\text{SnHCO}_2]^+$, $\text{Sn}(\text{HCO}_2)_2$, $[\text{Sn}_2(\text{HCO}_2)_5]^-$, in formate and $[\text{Sn}(\text{CH}_3\text{CO}_2)]^+$, $\text{Sn}(\text{CH}_3\text{CO}_2)_2$, $[\text{Sn}_2(\text{CH}_3\text{CO}_2)_5]^-$ and $[\text{Sn}_3(\text{CH}_3\text{CO}_2)_7]^-$ in acetate solutions. It has been suggested that the ions present in citric acid solution are $[\text{Sn}(\text{C}_6\text{H}_5\text{O}_7)]^-$, $[\text{Sn}(\text{OH})(\text{C}_6\text{H}_5\text{O}_7)]^{2-}$ and $[\text{Sn}(\text{C}_6\text{H}_5\text{O}_7)_2]^+$, and that 1:1:1 tin(II)–M–citrate or tartrate chelates are formed in solutions containing Sn(II) with $\text{M}=\text{Fe(III)}$ and Cu(II) . There is some evidence for complex formation in solutions of Sn(II) in mineral oxyacids. Complexes of the type $[\text{Sn}(\text{HSO}_4)]^+$, $\text{Sn}(\text{HSO}_4)_2$, SnSO_4 and $[\text{Sn}(\text{SO}_4)_2]^{2-}$ have been reported, and there is evidence for a number of pyrophosphate complexes in solutions containing tin(II) and pyrophosphate ions. The stable species in phosphorous acid solutions is $[\text{Sn}(\text{HPO}_3)_3]^{4-}$.

The main species present in alkaline Sn(II) solutions is the $[\text{Sn}(\text{OH})_3]^-$ anion, but there is also evidence for the polynuclear ion $[\text{Sn}_2(\text{OH})_4\text{O}]^{2-}$ in which the stable pyramidal Sn(II) environment would be maintained by a bridging oxygen atom. The predominant basic species in Sn–OH solutions at low pH is $[\text{Sn}_3(\text{OH})_4]^+$, and the basic tin(II) salts precipitated at about pH 2 are derivatives of this ion or of a closely related, often partially dehydrated species.

A number of tin(II) compounds are water soluble. The solutions are susceptible to hydrolysis giving hydrous tin(II) oxide and to oxidation to Sn(IV). The stability of the solutions depends upon the nature of the anions present and the pH. Solutions containing anions such as F^- or CH_3CO_2^- which form strong complexes with Sn(II) are relatively stable to hydrolysis and oxidation. Ease of oxidation increases with pH, and in very alkaline solutions spontaneous disproportionation to Sn and Sn(IV+) can occur. Tin(II) fluoride, SnF_2 , and chloride, SnCl_2 , are very soluble in water (SnCl_2 , 83.9 g in 100 ml H_2O at 0°C ; SnF_2 , 41 g in 100 ml at 25°C) and the solubilities (g (100 ml)^{-1} of solution) of some other tin(II) compounds are NH_4SnF_3 (59 at 25°C), SnSO_4 (35.2 at 20°C) and $\text{Sn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$ (1.9 at 25°C). Some Sn(II) compounds dissolve in non-aqueous media. Anhydrous SnCl_2 is readily soluble in acetone, glycol, methanol, pyridine and tetrahydrofuran, whilst $\text{Sn}(\text{NCS})_2$ is soluble in ethanol, $\text{Sn}(\text{HCO}_2)_2$ in propylene glycol, and SnBr_2 in alcohol, tetrahydrofuran and pyridine. The main complex species in these solutions is probably $[\text{SnX}_2 \cdot \text{ligand}]$ where the monodentate donor atom completes the pyramidal three-coordination of tin. Many solid derivatives of the type $[\text{SnX}_2 \cdot 2 \text{ ligand}]$ are known, but only one of the ligand atoms is

normally bonded to the tin, the other ligand molecule being present only for lattice packing purposes. Sn(II) is also stable in acetonitrile solutions in which the complex cations, $[\text{Sn}(\text{CH}_3\text{CN})_n]^{2+}$ ($n=2, 3, 6$) are said to exist. It is also likely that the ion $[\text{Sn}(\text{NH}_2)_3]^-$ is present in solutions of Sn(II) in liquid ammonia.

3.1.2 Structures of tin(II) compounds

The most important aspect of tin(II) chemistry that has been studied over the past 10 to 20 years has been concerned with non-bonding electron pair effects [2–4]. Particular attention has been paid to the distortion of tin(II) environments by the non-bonding electron pair and to compounds in which the non-bonding electrons are delocalized in solid state bands or clusters.

Surveys of the literature [2, 3, 5] on known crystal structures of tin(II) compounds show that the tin atoms are nearly all in low symmetry, non-bonding electron pair-distorted environments. There are, however, a number of compounds in which the distorting effects of the non-bonding orbitals are reduced or eliminated by solid-state effects. Although the detailed distribution of the atoms around tin(II) in the solid state can be complicated, most of them can be described in terms of the environments illustrated by structures (7)–(12) in Chapter 2. The most common tin(II) environment is a trigonal pyramidal arrangement of three nearest-neighbour tin–ligand bonds with three longer essentially non-bonding contacts completing a distorted octahedral coordination. These longer contacts arise because close approach of ligands to the tin is prevented by the non-bonding electron pair orbital in the direction in which it points.

A large number of tin(II) compounds contain tin atoms with pyramidal three-coordination. Tin(II) sulphate [6], for example, has three short Sn–O bonds (2.25–2.27 Å) in a pyramidal arrangement with three longer Sn–O distances (2.92–2.99 Å) completing a distorted octahedral coordination. Other tin(II) compounds [5] that have tin in this type of site include monoclinic SnF_2 , NH_4SnF_3 , NaSn_2F_5 , $\text{Sn}_2\text{F}_3\text{Cl}$, $\text{Sn}_3\text{F}_5\text{Br}$, $\text{Sn}_3\text{F}_3\text{PO}_4$, SnCl_2 , $\text{KCl}\cdot\text{SnCl}_3\cdot\text{H}_2\text{O}$, monoclinic CsSnCl_3 , $\text{SnCl}(\text{H}_2\text{PO}_2)$, $\text{K}_2\text{Sn}_2\text{O}_3$, $\text{Sn}_3(\text{PO}_4)_2$, SnHPO_4 , $\text{Sn}_2(\text{OH})\text{PO}_4$, $\alpha\text{-SnWO}_3$, $\text{KSn}(\text{HCO}_2)_3$, $\text{Ca}[\text{Sn}(\text{CH}_3\text{CO}_2)_3]_2$, SnHPO_3 , SnFPO_3 , SnS , BaSnS_2 , $\text{Sn}(\text{NCS})_2$, $\text{Sn}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$ and $[\text{CH}_3\text{B}\{\text{NSi}(\text{CH}_3)_3\}_2\text{Sn}]_2$. The structures of the bromostannates(II), $\text{NH}_4\text{Br}\cdot\text{NH}_4\text{SnBr}_3\cdot\text{H}_2\text{O}$ and $[\text{C}_3\text{H}_{12}\text{N}][\text{SnBr}_3]$ have recently been determined [7]. Both contain the trigonal pyramidal SnBr_3^- ion and the structure of the latter is shown in Figure 3.1

The structure of $\text{Sn}_3\text{F}_5\text{Br}$ (Figure 3.2) shows how the pyramidal three-coordination is maintained by bridging atoms in the formation of a tin(II) fluoride cationic network [8]. It is interesting that the trigonal pyramidal tin sites are also maintained in the formation of clusters [9] such as $[\text{Sn}_3(\text{OH})_4]^{2+}$ in $[\text{Sn}_3(\text{OH})_4][\text{NO}_3]_2$. Evidence [10] for the predominance of trigonal

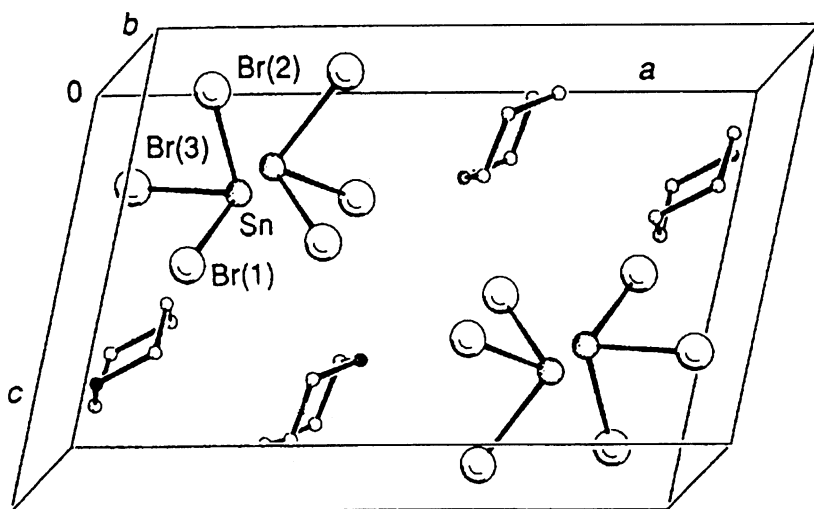


Figure 3.1 The structure of $[\text{C}_5\text{H}_{12}\text{N}][\text{SnBr}_3]$.

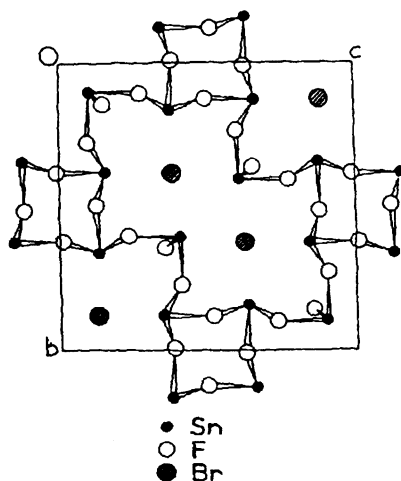


Figure 3.2 (100) Projection of the unit cell of Sn_3BrF_5 . (Reproduced by permission from Ref. 8.)

pyramidal environments in tin(II) chemistry, even in the presence of some potentially bidentate ligands, comes from the structure determination of potassium hydrogen bis(maleato)stannate(II) in which the discrete ions $[\text{Sn}(\text{CHCO}_2\text{:CHCO}_2)(\text{CHCO}_2\text{:CHCO}_2\text{H})]_2^{2-}$ are found. These ions have tin(II) in a trigonal pyramidal environment with two Sn–O bonds to an anisobidentate maleate ligand and one Sn–O bond to a terminal unidentate monoprotofemaleate ligand. Table 3.1 lists the bond length and pyramidal

Table 3.1 Bond lengths and angles in tin(II) materials with [SnX₃] sites

Compound	Sn	X	Bond lengths (Å)			Next nearest	Sn-X	Bond angles (°)		Ref.
			1	2	3					
Co(SnF ₃) ₂ ·6H ₂ O	Sn1	F	2.03	2.05	2.06	3.26	Sn-F	84.1	84.1	11
Ni(SnF ₃) ₂ ·6H ₂ O	Sn1	F	2.04	2.05	2.06	3.26	Sn-F	84.8	85.4	12
Zn(SnF ₃) ₂ ·6H ₂ O	Sn1	F	2.04	2.06	2.05	3.32	Sn-F	85.4	84.4	13
Cd(SnF ₃) ₂ ·6H ₂ O	Sn1	F	2.04	2.06	2.05	3.36	Sn-F	84.2	84.5	13
[N ₂ H ₄][SnF ₃] ₂	Sn1	F	2.10	2.05	2.08	2.66	Sn-F	82.6	82.0	14
K(Co(NH ₃) ₆ (SnF ₃) ₂ (NO ₃) ₂ ·0.5H ₂ O	Sn1	F	2.07	2.03	2.03	2.92	Sn-F	85.2	85.2	15
	Sn2	F	2.07	2.05	2.05	2.90	Sn-F	86.7	86.7	
	Sn3	F	2.05	2.03	2.04	2.94	Sn-F	86.6	86.5	
	Sn4	F	2.00	2.02	1.99	2.93	Sn-F	85.0	88.6	
	Sn1	F	2.14	2.28	2.16	2.39	Sn-F	78.6	82.0	16
[Sn ₆ F ₁₀][NbOF ₃]	Sn2	F	2.18	2.13	2.06			87.7	80.6	
	Sn3	F	2.08	2.18	2.19	3.01	Sn-F	86.2	81.2	
	Sn1	F	2.08	2.10	2.12	2.98	Sn-F	78.9	84.7	17
Sn ₂ F ₃ BF ₄	Sn2	F	2.07	2.10	2.10	2.96	Sn-F	81.6	86.4	
	Sn1	F	2.16	2.18	2.07	3.01	Sn-F	76.6	81.3	18
	Sn2	F	2.15	2.14	2.05	2.54	Sn-F	80.0	80.1	
(Sn ₆ F ₁₀)TiF ₆	Sn3	F	^a							
[C ₅ H ₁₂ N][SnCl ₃]	Sn1	Cl	2.53	2.55	2.56	3.33	Sn-Cl	88.6	88.8	19
	Sn1	Cl	2.55	2.55	2.55	3.16	Sn-Cl	88.1	88.1	19
	Sn1	Cl	2.55	2.56	2.56	3.22	Sn-Cl	88.1	88.5	20
	Sn1	Br	2.72	2.72	2.73	3.40	Sn-Br	89.0	89.0	19
	Sn1	Br	2.71	2.72	2.72	3.40	Sn-Br	89.3	89.8	19
[C ₅ H ₁₂ N][SnBr ₃]	Sn1	O	2.20	2.20	2.21	2.64	Sn-O	79.7	79.7	10
	Sn1	O								
KSn(CHCOO:CHCOO)(CHCOO:CHCOOH)	Sn1	O								
	Sn1	O								

$\text{Sn}_3(\text{OH})_4(\text{NO}_3)_4$	Sn1	O	2.16	2.15	2.35	71.8	72.4	84.4	9
	Sn2	O	2.15	2.14	2.30	71.3	73.6	83.3	
	Sn3	O	2.18	2.20	2.13	72.8	75.1	83.7	
$\text{K}_2\text{Sn}_2[\text{CH}_2(\text{CO}_2)_2]_3 \cdot \text{H}_2\text{O}$	Sn1	O	2.18	2.18	2.20	83.7	84.0	74.6	21
	Sn2	O	2.16	2.21	2.24	Sn-O	83.3	78.2	73.2
	Sn1	O	2.08	2.10	2.10	Sn-Li	79.7	80.1	97.6
$[\text{Li}(\text{OBu})_3\text{Sn}]_2$	Sn1	O	2.10	2.11	2.11	Sn-C	83.4	83.5	93.5
$[\text{Na}(\text{OBu})_3\text{Sn}]_2$	Sn1	O	2.06	2.07	2.07	Sn-K	81.5	90.7	91.9
$\text{K}(\text{OBu})_3\text{Sn}$	Sn1	O	2.04	2.04	2.04	Sn-Rb	96.5	96.6	96.6
$\text{Rb}_2\text{Sn}_2\text{O}_3$	Sn1	O	2.02	2.04	2.04	Sn-Sn	96.0	96.0	96.7
$\text{Cs}_2\text{Sn}_2\text{O}_3$	Sn1	O	2.02	2.04	2.04	Sn-Na	98.5	99.5	99.7
$\text{Na}_4[\text{SnO}_3]$	Sn1	O	2.28	2.39	2.42	Sn-O			30
SnMo_5O_8	Sn1	O	2.15	2.15	2.17	Sn-C	78.3	81.5	86.9
$[\text{NH}_4][\text{Sn}(\text{OCOCH}_2\text{Cl})_3]$	Sn1	O	2.11	2.12	2.17	Sn-O	83.6	84.6	89.8
$[\text{NH}_4]_2\text{Sn}(\text{HPO}_3)_2$	Sn1	S	2.62	2.66	2.66	Sn-S	89.0	89.0	89.0
$\alpha\text{-SnS}$	Sn1	S	2.65	2.65	2.77	Sn-S	83.6	83.6	83.6
Sn_2S_3	Sn1	S	2.63	2.64	2.74	Sn-S	85.4	86.8	92.0
$\text{Ga}_2\text{Sn}_2\text{S}_5$	Sn2	S	2.64	2.69	2.75	Sn-S	82.9	89.4	92.7
	Sn1	S	2.56	2.57	2.75	Sn-S	90.2	91.4	94.6
BaSn_2S_3	Sn2	S	2.59	2.64	2.64	Sn-S	91.0	91.0	95.5
	Sn3	S	2.55	2.59	2.68	Sn-S	90.2	92.8	97.5
	Sn4	S	2.44	2.71	2.71	Sn-S	92.0	95.6	95.6
$[\text{Sn}(\text{NMe}_2)_2]_2$	Sn1	N	2.07	2.67	2.67	Sn-C	80.0	99.8	100.4
			2.98						36

^aFour-coordinated SnX_4 site; see Table 3.3.

bond angle data for crystal structures of tin(II) compounds, determined since 1980, which contain three-coordinated $[\text{SnX}_3]$ environments. Table 3.2 contains the bond length and angle data for compounds with trigonal pyramidal $[\text{SnX}_2\text{Y}]$ sites. Details of tin(II) structures with pyramidal three-coordinated sites that were published before 1980 are to be found in Ref. 5. Other structures determined since 1980 are found in Refs 22–26.

The second most common type of tin(II) environment has a distorted four coordinated pyramidal arrangement of atoms around the tin. The main structural feature found in almost all four-coordinated tin environments is the existence of two bonds of considerably greater length than those normally found in tin(II) compounds. The environment of tin in $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$ shown in Figure 3.3 provides a good example of this type of tin(II) site [38]. The tin atoms are also in distorted four-coordinated environments in the tin(II) oxyhydroxide, $\text{Sn}_6\text{O}_4(\text{OH})_4$ in which each tin is bonded to two bridging oxide oxygens and to two bridging hydroxyl groups [39]. Table 3.3 provides bond length and angle data for tin(II) structures, determined since 1980, which have distorted four-coordinated tin(II) environments. Again examples of structures determined before 1980 are to be found in Ref. 5. Table 3.4 contains similar data for compounds with $[\text{SnX}_3\text{Y}]$ and $[\text{SnX}_2\text{Y}_2]$ sites. In some tin(II) compounds the distorted tin(II) environments have more complicated geometries, including those for $\beta\text{-SnS}$ and $\beta\text{-SnSe}$ [53], $\text{Sn}_2\text{Sb}_2\text{S}_5$ [54], and $\text{Bi}_x\text{Sb}_{2-x}\text{Sn}_2\text{S}_5$ [55].

It has also been reported that tin is found in eight-coordinated environments in $\text{Sn}_2\text{P}_2\text{S}_6$ (Sn–S distances 2.91–3.23 Å) and in $\text{Sn}_2\text{P}_2\text{Se}_6$ (Sn–Se bond distances 3.00–3.31 Å) [56, 57]. Although most tin(II) compounds contain the element in a lone-pair distorted site, there are a number of examples where the tin is in a high symmetry undistorted site. Compounds with high symmetry tin(II) sites include CsSnBr_3 [58], the high temperature modifica-

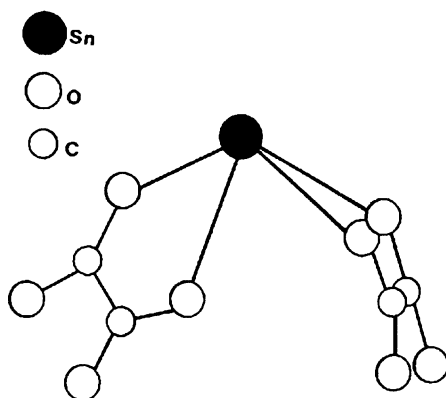


Figure 3.3 The environment of tin in $\text{Na}_2(\text{C}_2\text{O}_4)_2$. (Reproduced by permission from Ref. 38.)

Table 3.2 Bond lengths and angles in tin(II) materials with [SnX₂Y] sites

Compound	Bond lengths (Å)					Bond angles (°)		Ref.	
	Sn	X	Y	X	Y	Next nearest	Sn-X		
Sn(tu)Cl ₂	Sn1	Cl	S	2.49	2.61	2.70	3.19	Sn-Cl 88.0 90.6 93.5	21
NH ₄ Br·NH ₄ SnBr ₂ Cl·H ₂ O	Sn1	Br	Cl	2.70	2.72	2.56	3.28	Sn-Br 87.3-90.5	20
Sn(NSiMe ₃) ₂ μOBu ₂	Sn1	O	N	2.17	2.17	2.13	4.59	Sn-N 72.1-103.7	37

Table 3.3 Bond lengths and angles in tin(II) materials with [SnX₄] sites

Compound	Bond lengths (Å)					Bond angles (°)		Ref.
	Sn	X	1	2	3	4	Next nearest	
(Sn ₆ F ₁₀)TiF ₆	Sn1	F	^a					18
	Sn2	F	^a					
	Sn3	F	2.16	2.17	2.26	2.41	2.92	
RbSn ₂ Br ₅	Sn1	Br	2.76	2.76	3.11	3.11	3.49	Sn-F 78.0-150.8
InSn ₂ Br ₅	Sn1	Br	2.79	2.79	3.06	3.06	3.41	Sn-Br 79.0 91.8 148.1 40
InSn ₂ I ₅	Sn1	I	3.05	3.05	3.27	3.27	3.62	Sn-Br 78.2 91.3 146.0 41
Sn(CH ₂ C ₂ O ₄)	Sn1	O	2.18	2.23	2.26	2.56	2.95	Sn-I 77.7 90.9 144.7 41
Sn(H ₃ PO ₃) ₂	Sn1	O	2.16	2.16	2.35	2.35	3.36	Sn-O 77.1-78.3 42
SnC ₂ H ₄ O ₂	Sn1	O	2.07	2.11	2.31	2.34	2.95	Sn-O 79.0-151.4 19
Sn(S ₂ O ₃) ₂	Sn1	O	2.24	2.26	2.26	2.32	3.39	Sn-C 67.2-141.4 43
Sn ₂ (OSO ₄)	Sn1	O	2.15	2.26	2.35	2.56	2.83	Sn-O 72.6-78.9 44
	Sn2	O	2.14	2.23	2.34	2.52	2.91	Sn-O 71.1-142.9 45
Sn[C ₅ (COOMe) ₃] ₂	Sn1	O	2.24	2.24	2.27	2.27	2.93	Sn-O 78.0-158.4 46
Sn(OSO ₂ F) ₂	Sn1	O	2.40	2.34	2.43	2.35	2.69	Sn-O 69.1-144.2 47
Sn ^{II} Sn ^{IV} O ₃ (CF ₃ CO ₂) ₈	Sn1	O	2.12	2.23	2.33	2.53	2.94	Sn-O 74.8-146.9 48
In ₅ Sn ₁₀ S ₇	Sn1	S	2.99	2.99	3.02	3.02	3.24	Sn-O 66.1-153.0 48
Tl ₃ Sn ₂ S ₃	Sn1	S	2.68	2.89	2.93	3.11	3.44	Sn-S 79.8-136.7 87
Eu ₂ SnS ₅	Sn1	S	2.37	2.37	2.43	2.46	3.50	Sn-S 79.4-162.0 88
	Sn2	S	2.32	2.35	2.74	2.74	3.01	Sn-S 95.5-143.6 89
Sn[S ₂ P(OC ₄ H ₉) ₂] ₂	Sn1	S	2.62	2.65	2.83	3.04	3.39	Sn-S 93.4-167.6 90
Sn[C(PMe ₃) ₃] ₂	Sn1	P	2.60	2.60	2.79	2.84	3.27	Sn-S 74.2-170.7 91
							Sn-C 62.9-142.5	

^aSnX₃ coordinated tin site; see Table 3.1

tion of CsSnCl_3 [59], phases in the system $\text{CsSnBr}_{3-x}\text{Cl}_x$ [59], Cs_4SnBr_6 [60], SnTe [2] and the high temperature forms of SnS [2] and SnSe [2].

In all of these compounds the high symmetry arises because of delocalization of the non-bonding electrons into solid state bands. Similar solid state effects are also seen in blue-black tin oxide in which the tin atom, although in a distorted environment, has regular square-pyramidal coordination of oxygen atoms. Studies on the reasons for the formation of high symmetry tin(II) sites have provided some of the more important advances in our knowledge of the effects of non-bonding electron pairs on the chemistry of Main Group elements in recent years, and are discussed in the next section of this chapter.

A recent series of publications [61–63] has described the crystal structures of a number of complexes formed between tin(II) compounds and nickel, cobalt, copper and zinc salicylideneamine complexes. The transition metal complexes have a trapezium arrangement of oxygen atoms enabling them to act as effective tetradentate donor ligands to give both 1:1 and 2:1 acid:base addition complexes with SnX_2 ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ and NCS). The tin atoms in these complexes are bonded to four oxygen donor atoms from the salicylideneamine groups. In some complexes, for example, $\{\text{Sn}\cdot\text{Ni}[(3\text{-MeOs}al\ 1,3pn)(\text{H}_2\text{O})_2]\}\text{Cl}_2$ tin is only bonded to oxygen atoms. In this chloride there are two $\text{Sn}-\text{O}$ bonds of 2.18 \AA and two of 2.46 \AA but the $\text{Sn}\cdots\text{Cl}$ distance at 2.97 \AA is very long and exceeds the sums of both the covalent (2.39 \AA) and ionic (2.81 \AA) $\text{Sn}-\text{Cl}$ radii. In other complexes, for example $\{\text{SnBr}\cdot[\text{Ni}(3\text{-MeOs}al\ 1,3pn)(\text{MeCN})(\text{H}_2\text{O})]\}\text{Br}$ (Figure 3.4), the tin is bonded to four oxygen atoms and to a short $\text{Sn}-\text{X}$ bond. In the complex shown in Figure 3.4 the four $\text{Sn}-\text{O}$ bond distances to $\text{O}(1)$, $\text{O}(2)$, $\text{O}(3)$ and $\text{O}(4)$ are 2.189 , 2.199 , 2.642 and 2.650 \AA , respectively. There is one short $\text{Sn}-\text{Br}$ bond

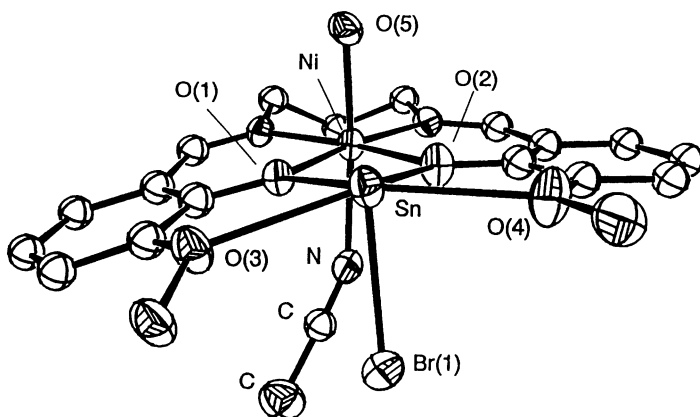


Figure 3.4 The structure of $[\text{SnBr}\cdot[\text{Ni}(3\text{-MeOs}al\ 1,3pn)(\text{MeCN})(\text{H}_2\text{O})]]\text{Br}$.

(2.710 Å) to bromine and the next nearest Sn...Br distance to Br(2) is at 3.724 Å. The question then arises as to whether these short Sn–X bonds can be described as giving rise to monohalostannate(II) ions in spite of the strong bonds that exist between the tin and the oxygen donor.

The details of the Sn–O and Sn–X bonds in the tin(II)–metal salicylideneamine complexes are given in Table 3.5. One of the noteworthy features of Ni(3-MeOsal 1,3pn) as a ligand in tin(II) and tin(IV) chemistry is the fact that thiocyanate groups on tin tend to migrate to nickel on adduct formation. This has been noted, for example, in the adduct $\text{SnMe}_2\cdot\text{Ni}(3\text{-MeOsal } 1,3\text{pn})(\text{NCS})_2$. In fact thiocyanate migration is strongly favoured over halide migration and this provides a novel route to the formation of monohalostannate(II) cations via the replacement of one halide by thiocyanate and the latter migrating to nickel.

In addition to the complexes listed in Table 3.5, a number of other adducts of tin(II) with metal salicylideneamines have been described. For example, the reaction of $\text{SnBu}_2(\text{NCS})_2$ with $[\text{SnBr}\cdot\text{Ni}(3\text{-MeOsal } 1,3\text{pn})(\text{MeCN})(\text{H}_2\text{O})]\text{Br}$ leads to the formation of a most unusual adduct, the structure of which is composed of two types of dimeric unit. In one dimeric unit all thiocyanate groups are on nickel and the tin atoms are disordered with equal site occupancies over two positions, one of which is essentially in the plane of the four Schiff-base oxygens. The disorder of tin appears to be a response to the disorder of the bridging water molecule. In both positions, tin forms bonds with all four Schiff-base oxygens, while at the same time there is a strong donor bond with the bridging water molecule. The role of water is quite complex since not only does it form bonds to tin, but it is probably also involved in hydrogen bonding interactions with the Schiff-base oxygen atoms. It is these interactions of the water molecule which hold the dimer together. Within the second dimer there are only two thiocyanate groups, one attached to each nickel. In this instance the dimer is held together exclusively by a bridging oxygen atom. It is suggested that the latter dimer contains the μ -oxo ditin(II) cation $(\text{Sn}=\text{O}-\text{Sn})^{2+}$. The μ -oxo and μ -aqua dimers alternate along an infinite chain polymer which results from the sulphur atom of a thiocyanate attached to nickel in the μ -aqua dimer forming a donor bond to a nickel of the μ -oxo dimer.

There is a suggestion from the structures described that tin, when bound to

Table 3.5 Tin(II) adducts with nickel salicylideneamine complexes

Compound	Sn–O				Sn–X	Sn...X
$\{\text{Sn}[\text{Ni}(3\text{-MeOsal } 1,3\text{pn})](\text{H}_2\text{O})_2\}\text{Cl}_2$	2.18	2.18	2.46	2.46		2.97
$[(\text{SnBr})\cdot\text{Ni}(\text{L})(\text{MeCN})(\text{H}_2\text{O})]\text{Br}$	2.19	2.20	2.64	2.65	2.71	3.72
$\{\text{SnF}\cdot\text{Ni}(\text{L})(\text{H}_2\text{O})\}_2\text{SnF}_6$	2.19	2.19	2.64	2.69	2.02	
$\text{SnCl}\cdot[\text{Ni}(\text{L})(\text{NCS})(\text{MeOH})]$	2.16	2.23	2.55	2.69	2.51	
$\{\text{Sn}(\text{NCS})\cdot[\text{Ni}(\text{L})(\text{NCS})(\text{MeCN})]\}_2$	2.22	2.22	2.63	2.67	2.21	3.68 (to S)

$\text{H}_2\text{L} = N,N'-1,3\text{-propylenebis-3-methoxysalicylideneamine}$.

the Schiff-base oxygens, is capable of forming only one additional strong bond. However, the structure of the tin acetate adduct shows that this is not necessarily the case. The Sn–O bonds to the salicylaldehyde oxygen donors are 2.17, 2.19, 2.66 and 2.74 Å but the acetate groups bridge the nickel and tin atoms in a similar fashion and the acetate oxygens form reasonably short Sn–O bonds with lengths of 2.31 and 2.36 Å. When the adduct is crystallized from an acetic acid–methanol mixed solvent system, a molecule of acetic acid takes part in a strong hydrogen bonding interaction with an acetate oxygen bonded to tin with the interesting effect that the Sn–O bond length involving this oxygen is dramatically increased to 2.61 Å while the Sn–O bond length involving the second acetate oxygen undergoes a contraction to a value of 2.27 Å.

3.1.3 Bonding in tin(II) compounds [2, 3]

One of the problems associated with the description of bonding in tin(II) compounds is the difficulty of including in any model those derivatives that have tin(II) in undistorted regular octahedral sites and have unusual solid state properties. Covalent models have to assume that the non-bonding electrons in high symmetry structures are in stereochemically inactive orbitals, that is, that they behave essentially as a $5s^2$ pair. An alternative suggestion [64] is that, since the ns orbital (A_{1g}) of the central atom plays little part in the bonding, the extra pair of electrons can be accommodated in the A_{1g} anti-bonding molecular orbital, without distorting the O_h symmetry. None of the models based on covalency can, however, explain why non-bonding orbitals can be stereochemically active in one site and inactive in a similar site in another compound. More importantly, none of these approaches accounts for the unusual optical and electrical solid state properties associated with high symmetry tin(II) environments. The electrostatic arguments of Orgel [65], on the other hand, do predict that distortion will be greatest for tin(II) bonding to light atoms and least for tin(II) bonding to heavy atoms. This is consistent with the observation that the most distorted tin(II) sites are generally found when tin is bonded to oxygen and fluorine atoms. Orgel's approach, however, suffers from the same disadvantage as the covalent approach insofar as localization of the description to crystal field effects on the tin atom alone necessarily means that the model cannot explain any three-dimensional solid state effects. The high symmetry tin(II) compounds are normally coloured and have interesting electrical and optical properties. For example, CsSnBr_3 crystallizes in an undistorted perovskite lattice. It is a black solid with a metallic lustre, an electrical conductor and a material which shows interesting photoemission effects. The ^{119}Sn Mössbauer spectrum of the material has a very narrow linewidth consistent with the undistorted octahedral symmetry of the tin atom, but its chemical shift ($\delta = 3.95 \text{ mm s}^{-1}$) is much lower than would be expected from a material with relatively long

Sn–Br bonds (2.94 Å). An explanation for the differences observed in the stereochemical activity of the lone pairs in tin(II) compounds can, however, be obtained by considering the energy levels of the bonding of orbitals of both tin and its ligands. Consideration of the overall symmetry of the lattice then enables us to extend the arguments used to account for the solid state effects in high symmetry tin(II) compounds.

A simple rationale for differences in the $s:p$ ratios in tin(II) compounds can be provided by consideration of orbital energy matching [2]. The rationale employs derivatives of the trihalogenostannate(II) ions (SnX_3^- ; X = F, Cl, Br, I) as examples and is shown to be entirely consistent with their structures and Mössbauer data [66]. The stereochemical activity of the tin non-bonding electron pair will depend on the directional tin $5p_z$ orbital character in the non-bonding lone-pair orbital and the Mössbauer parameters, in the Townes–Dailey approximation, on the fractional $5s$ and $5p$ character of the molecular orbitals. We have suggested [2] that, in order to form a strong a_1 bond, tin $5s$ and $5p_z$ orbitals will premix such that the energy of the hybrid orbital so formed will match that of the halogen np orbital. The binding energies of the tin $5s$ and $5p$ and halogen np orbitals are shown in Figure 3.5, and it can be seen that in order to obtain a good energy match with the appropriate halogen group orbital, the tin a_1 bonding orbital should contain high $5s$ character when bound to fluorine but high $5p_z$ character when bound to iodine. The nonbonding orbital (because of orthogonality requirements) thus contains high tin $5p_z$ and low $5s$ character in $[\text{SnF}_3]^-$. This orbital occupancy

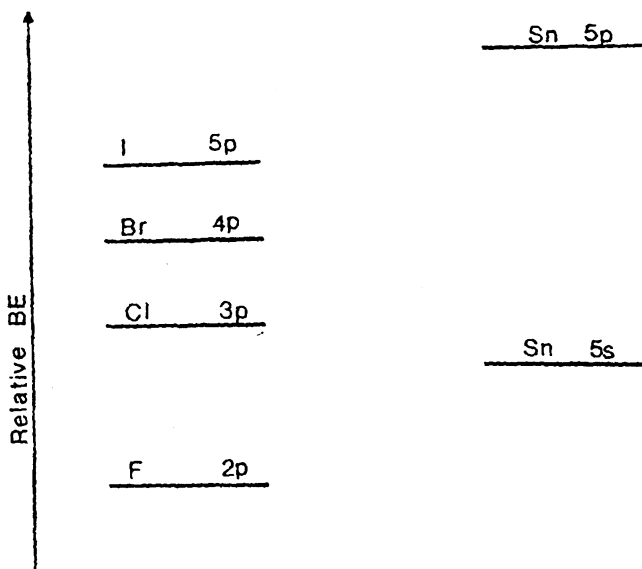


Figure 3.5 Relative binding energies of tin $5s$ and $5p$ and halogen np orbitals.

would lead to a highly directional lone pair containing high tin $5p_z$ character and hence distorted tin(II) environments, large negative Mössbauer quadrupole coupling constants and small isomer shifts for $[\text{SnX}_3]^-$ ions containing electronegative ligands such as fluorine. In contrast, for $[\text{SnX}_3]^-$ ions containing less electronegative ligands such as iodine, the lone pair would contain high tin $5s$ character and would therefore be much less stereochemically active, the isomer shifts would be large and the quadrupole coupling constants small. One of the strengths of the orbital matching model is the ease with which it can be extended to describe the bonding in and properties of the tin(II) compounds with high symmetry structures.

The increase in the tin $5s$ character of the non-bonding pair in going from fluorides to iodides is paralleled by a decrease in distortion. As the distortion decreases, it becomes possible to remove the distorting effects of the non-bonding electron pair by solid-state effects as well as by direct alteration in the p -character of the electrons in the orbital. The removal of distortion by solid state effects can be explained in terms of direct population of empty delocalized bands by the non-bonding electrons. This phenomenon is best illustrated by discussion of the undistorted perovskite, CsSnBr_3 . If we look at a projection of the perovskite lattice showing the positions of the tin and the bromine atoms, it is easy to see how a delocalized empty band system can arise from the mutual overlap of empty bromine $t_2 4d$ orbitals (Figure 3.6). Calculation of the size of the $5s^2$ orbital on the tin atom leads to the conclusion that there will be an overlap between the $5s^2$ orbital and the empty bromine $4d$ orbitals. It then becomes possible for the distortive effects of the non-bonding orbital to be reduced by the direct population of the solid state band with the non-bonding tin electrons. The vibrational spectra for the compound can only be ration-

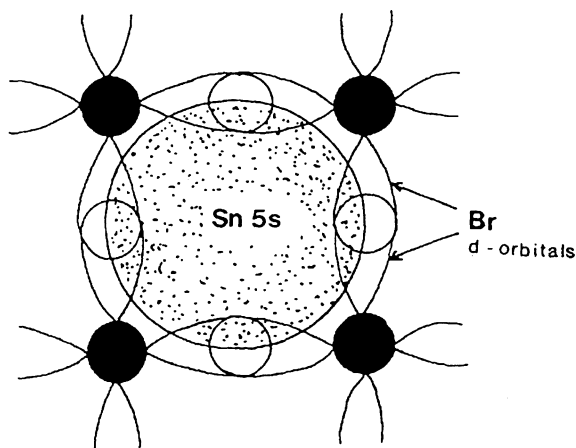


Figure 3.6 Overlap of tin $5s$ orbitals with bands formed from empty bromine orbitals leading to delocalization of tin electrons into solid state bands.

alized if Br–Br interactions such as those that would arise from population of the bromine $4d$ bands are considered. It seems to be particularly significant that $\text{Cs}_2\text{Sn}^{\text{IV}}\text{Br}_6$, which has a structure closely related to that of CsSnBr_3 , is white and shows none of the optical and electrical properties associated with CsSnBr_3 . The caesium and bromine atoms are in the same relative positions in both compounds, but in the tin(IV) complex only one-half of the perovskite tin sites are occupied. The cell volume for Cs_2SnBr_6 ($a = 10.8 \text{ \AA}$) is less than that for the corresponding number of caesium and bromine atoms in CsSnBr_3 ($a = 11.6 \text{ \AA}$). The tin(IV) complex must therefore contain a lower energy acceptor band like CsSnBr_3 but, unlike CsSnBr_3 , the complex has no high energy non-bonding electrons with which to populate these empty bands. For this reason Cs_2SnBr_6 , in common with similar hexabromo- and hexachlorostannates(IV), is white and insulating.

The concept of direct population of solid state bands can explain all of the apparently anomalous properties of CsSnBr_3 . Its undistorted perovskite structure must arise because the mutual overlap of the bromine $4d$ orbitals would be at a maximum in such a structure, and this in turn would permit maximum transfer of electron density from the potentially distorting non-bonding tin orbitals. The electrical properties of CsSnBr_3 must arise as a result of the population of the empty bromine t_2 bands with electrons from the tin atoms. The very low ^{119}Sn Mössbauer chemical isomer shift for CsSnBr_3 and its variation with temperature arise because tin s -electron density is lost to the solid state band structure and because the amount of loss is at a maximum at about room temperature (section 3.1.4). This loss of s -electron density is at the same time reflected in the change in electrical conductivity of the material, in which a decrease in the chemical isomer shift corresponds to an increase in the conductivity (Table 3.6).

The results of direct population also explain the following optical properties of CsSnBr_3 [67]. At 300 K, CsSnBr_3 shows an absorption edge at 1.80 eV. Excitation to high energy of this edge produces an intense red emission with a maximum at 1.78 eV and a symmetrical Lorentzian shape. At higher energies

Table 3.6 Variable temperature ^{119}Sn Mössbauer parameters and electrical conductivity for CsSnBr_3

Temperature (K)	δ^a (mm s^{-1})	Γ (mm s^{-1})	Conductivity ($\Omega^{-1} \text{ cm}^{-1} \times 10^4$)
4.2	4.14	1.00	
80	3.97	0.84	7.91
295	3.89	0.77	9.34
295 (^{119}Sn -enriched)	3.89	0.77	9.34
323 (^{119}Sn -enriched)	3.85	1.00	8.66
348 (^{119}Sn -enriched)	3.89	1.28	7.85
383 (^{119}Sn -enriched)	4.05	1.30	
418 (^{119}Sn -enriched)	4.23	1.38	

^aRelative to BaSnO_3 .

the intensity of this band decreases rapidly until at 430 K it reaches 1% of its 300 K intensity. This high temperature quenching may be associated with the loss of the Sn(II) Mössbauer resonance and its replacement with a Sn(IV) resonance at *c.* 400 K. As the temperature is reduced to below ambient, the luminescence spectrum shows the usual sharpening and shift to lower energy, the band maximum being at 1.72 eV at 80 K. Further cooling results in a decrease in intensity of this band and its replacement by a broader asymmetric feature with a maximum at 1.75 eV. This band and the emission at higher temperatures has a lifetime of less than 10^{-6} s. At 10 K a second intense emission is observed at 1.16 eV. This second band has not been observed at higher temperatures with optical excitation, but it can be observed at room temperature using electron beam excitation. No photoconductivity was detectable.

The similarity of the position of the absorption edge of CsSnBr₃ to the onset of the emission band indicates that the optical properties in the visible region are to be associated with direct band-to-band transitions. The bandwidths and lifetimes are consistent with this. The band gap (1.7 eV) is much larger than that responsible for the change in electrical conductivity with temperature (0.34 eV). Failure to observe photoconductivity supports the existence of at least two bands.

A proposed band model which explains the observed electrical, and optical properties of CsSnBr₃ as well as Mössbauer data, is shown in Figure 3.7. In this model the tin 5s orbitals form a narrow band which overlaps with an empty band formed by the bromine 4d orbitals in the forbidden energy region, allowing direct population of the empty band by the tin 5s electrons.

The high symmetry, solid state environment for tin in its lower oxidation state is only found for those compounds in which the distorting effect of the non-bonding electron pair can be reduced by causing the electrons to populate a low energy delocalized band in the structure [67–69]. This model can be

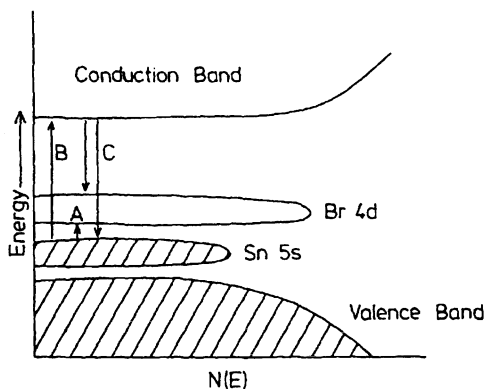


Figure 3.7 Band structure of CsSnBr₃.

extended to explain colour in tetragonal SnO and other materials which have relatively short metal-metal contacts because, in these cases, the ns^2 element is not only supplying the donor electrons but also forming the band by mutual overlap of its empty d -orbitals.

Recent work has shown that the non-bonding orbitals can also be delocalized in clusters. For example, $K_3Sn_2(SO_4)_3Br$ consists [70] of a three-dimensional network of tin atoms and bridging sulphate groups. The tin atoms occupy only two-thirds of the symmetry-related positions available for them in the network, and the remaining one-third are taken up by potassium atoms. The remaining potassium and halogen atoms lie in special positions and are discrete ions. The Sn-O and Sn-X bond lengths are unusually long and the Mössbauer chemical shift is unexpectedly low in view of the length of the bonds around the tin (section 3.1.4). Taken with the crystal structure, these observations are consistent with cluster formation of tin atoms around the bromine atoms (Figure 3.8). Because of the distribution of Sn-O bonds around the tin atoms, the non-bonding electron pairs must be directed towards the centre of the octahedron and the bromine atom. These non-bonding electron pair orbitals must then overlap empty d -orbitals of adjacent tin atoms giving rise to the weak Sn-Sn cluster interactions and Sn-Sn distances in the range 4.62–4.64 Å. The fact that the non-bonding electron pairs are all directed towards the centre of an octahedron must lead, even if they are being delocalized into cluster orbitals, to a build-up of electron density. In this respect it is interesting that the clusters contain only four tin

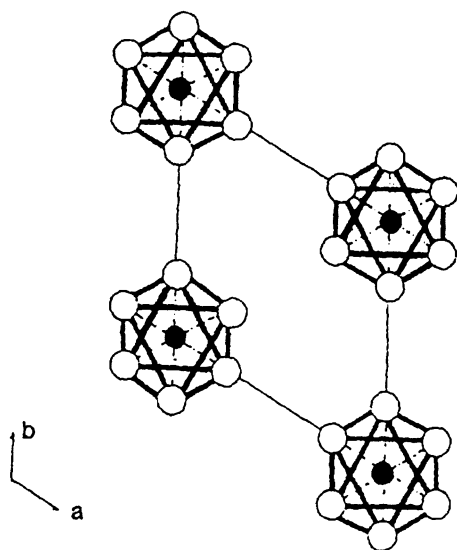


Figure 3.8 Cluster formation in $K_3Sn_2(SO_4)_3X$ species.

atoms, the remaining two atoms being potassium. The effect of the potassium atoms and possibly the central halogen atom must be to reduce the electron build-up within the octahedron and to stabilize the cluster. The effects of the cluster electron-delocalization interactions would be threefold: (1) to remove the distorting effects of lone-pair orbitals pointing towards a halide ion; (2) to delocalize the tin electron density into cluster orbitals giving rise to its anomalous ^{119}Sn Mössbauer chemical shift, and (3) to weaken the tin–ligand bond outside the cluster. Cluster formation of metal atoms around the halogens therefore provides an explanation for all the apparent anomalous structural and Mössbauer data for the $\text{K}_3\text{Sn}_2(\text{SO}_4)_3\text{X}$ compounds. Cluster formation involving tin(II) atoms is a novel example of the Sn–Sn interactions that have important consequences in certain tin(II) compounds. The types of Sn–Sn interactions range from dimer formation in $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ [71] where the stability and structure of the material arise from interactions between the lone pair of one tin atom with the empty orbital on the other tin atom in the dimer, to the interactions that account for the optical and electrical properties of compounds such as CsSnBr_3 and SnO where the non-bonding orbitals are delocalized into three-dimensional and adjacent-layer tin bands respectively. The Sn–Sn interactions in the $\text{K}_3\text{Sn}_2(\text{SO}_4)_3\text{X}$ clusters must be intermediate in nature between those of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ and the full delocalized systems. Another compound in which delocalization has been proposed is $\text{Cs}_2\text{Sn}_6\text{Br}_3\text{F}_{11}$ [49].

In the vapour state, tin(II) compounds of the type SnX_2 should have V-shaped angular structures, and it has long been known [1] that SnCl_2 and SnBr_2 do in fact have this type of lone-pair distorted structure. Recent work on the chemistry of molecular tin(II) compounds with bulky groups attached to the tin [72] has shown that $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is also a V-shaped angular structure with Sn–N bond lengths of 2.09 Å and a N–Sn–N bond angle of 96°. In the solid state this compound retains its monomeric molecular structure, although the N–Sn–N bond angle in the solid is widened to 100.47°. The molecule $\text{Sn}(\text{OC}_6\text{H}_2\text{MeBu}'_2)_2$ [73] is also a V-shaped monomer in the vapour phase. Gaseous tin(II) *tert*-butoxide is, however, a *trans* dimer with a very small endocyclic O–Sn–O angle (76°), while solid tin(II) (tri-*tert*-butyl)methoxide contains monomeric angular $[\text{Sn}(\text{OCBu}'_3)_2]$ molecules [74]. ^{119}Sn NMR can be used [74] to distinguish between compounds with a tin coordination of two and those in which the coordination is raised to three or four by intermolecular interactions.

3.1.4 Mössbauer spectroscopy and bonding in tin(II) compounds

The ^{119}Sn Mössbauer effect has proved to be a valuable tool in providing information on the ways in which tin uses its bonding electrons in tin(II) compounds. Mössbauer spectroscopy has, for example, been used to compare the covalent character of the bonds in different modifications of the

same material, e.g. CsSnCl_3 [75]. The Mössbauer data for adducts of normal tin(II) compounds and for tin(II) complexes show lower chemical shifts [2] than the corresponding parent tin(II) materials. This is to be expected, because of the greater *s*-electron involvement in the bonding of the complexes [1] and can be explained in terms of the change in bonding as the tin environment alters from SnX_2 to $[\text{SnX}_3]^-$ as the ligand X(3) forms a bond to tin creating a discrete group, and no longer acts as a bridge in a polymeric chain. The chemical shifts for MSn_2X_5 compounds such as NaSn_2F_5 ($\delta = 3.32 \text{ mm s}^{-1}$) are intermediate between that of SnX_2 and the corresponding trihalostannate(II) (for example SnF_2 , $\delta = 3.62 \text{ mm s}^{-1}$ and NaSnF_3 , $\delta = 3.12 \text{ mm s}^{-1}$). This is consistent with the presence of a bridging F atom in $[\text{Sn}_2\text{F}_5]^-$. The anomalous nature of the Sn(II)–F bond is clearly shown in the Mössbauer shift data for tin(II) fluorides and the fluorostannates(II) which are anomalously low, but which can be explained by high use of tin *s*-electron density in the bonding as predicted by the orbital energy matching concept (section 3.1.3).

It has been found that, as expected, formation of adducts of the type $\text{SnX}_2\text{--L}$ results in a lowering of chemical shifts when compared to their parent compounds. The strength of the tin–ligand bond can be inferred from the chemical shift for the complex, and from the difference between this value and the shift of the parent compound. The relatively small lowering in shift in going from the tin(II) halides, SnCl_2 , $\delta = 4.12 \text{ mm s}^{-1}$, SnBr_2 , $\delta = 3.98 \text{ mm s}^{-1}$, to the 1,4-dioxan complexes, $\text{SnCl}_2\text{--}1,4\text{-dioxan}$, $\delta = 3.71 \text{ mm s}^{-1}$, $\text{SnBr}_2\text{--}1,4\text{-dioxan}$, $\delta = 3.71 \text{ mm s}^{-1}$, for example, shows that the tin–ligand bonds are weak in these materials. It is, however, difficult to obtain detailed information on the relative acceptor strengths of all tin(II) compounds towards a given ligand because the chemical shifts, which measure total *s*-electron densities at the tin nucleus will also be very dependent on the atoms, other than the donor ligand atoms, bonded to the metal. The largest change in the chemical shift on complex formation occurs with the formation of the 1:1 adduct, addition of further ligand molecules to form polyligand complexes generally having a much smaller effect on the shift. These observations are consistent with the expected predominant monofunctional acceptor properties of tin(II) compounds.

There can be no general relationship between the chemical shifts and quadrupole splittings for tin(II) compounds because this would require a direct relationship between changes in *s*-electron density and changes in the imbalance of *p*-electron density. The presence of the non-bonding electron pair does not in itself appear to lead to an electronic imbalance. CsSnBr_3 , in which the tin is in a regular octahedral site, has a very narrow line as would be expected, and the $[\text{Sn}_2\text{F}_5]^-$ anion has a large quadrupole splitting because of the asymmetry of this ion and the nature of the Sn–F bond. The signs of the quadrupole coupling constants are positive for several bivalent tin compounds [75] which are consistent with the main contribution to the field

gradient arising from the *p*-electron excess in the non-bonding electron pair. However, in order to explore the relative sizes of quadrupole splittings in tin(II) compounds, it has been shown to be necessary to consider the *p*-electrons in the bonding orbitals as well as the non-bonding electron pair, because they too can have a considerable effect. It is significant that the orbital energy matching concept predicts that quadrupole splitting should be greatest for tin(II) bonded to light atoms such as fluorine or oxygen where high use of tin *s*-electrons in Sn–F and Sn–O bonds leaves *p*-electron density in the non-bonding electron pair, thus creating the *p*-electron imbalance responsible for the quadrupole splitting.

A considerable amount of attention has recently been given to the relationship between crystal structure and ^{119}Sn Mössbauer data. Two aspects of the relationship can be considered: (1) the general relationship between the main features of the structure of a tin(II) compound and its Mössbauer data, and (2) a specific relationship between Mössbauer chemical shifts and bond lengths. The Mössbauer parameters (Table 3.7) for the ternary halides SnXX' , $\text{Sn}_2\text{XX}'_3$ and $\text{Sn}_3\text{XX}'_5$ serve to illustrate the general relationship. The Mössbauer data for these compounds cannot be consistent with the presence of both Sn–X and Sn–X' sites and, although it is possible to devise a SnCl_2 -type structure with only one site for SnXX' and $\text{Sn}_2\text{XX}'_3$, the same cannot be done for $\text{Sn}_3\text{XX}'_5$. The crystal structure of Sn_3BrF_5 (Figure 3.2) is consistent with the Mössbauer data in that it is built up from a polymeric Sn–F cationic network with Br^- ions, not bonded to the tin, occupying spaces in the lattice to balance the charge. The tin sites in the ternary structure are not identical crystallographically, but are sufficiently alike to give similar Mössbauer resonances which appear as a quadrupole-split doublet. The crystal structure of Sn_2ClF_3 also comprises polymeric fluorotin cations and chloride anions, and is best represented as $[\text{Sn}_2\text{F}_3]_n^{n+}\text{Cl}_n^{n-}$ with no Sn–Cl bonds, in agreement with the Mössbauer data [5].

The Mössbauer isomer shift for $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ has a value just above that for α -tin – the borderline between Sn(II) and Sn(IV). The crystal struc-

Table 3.7 Mössbauer parameters of ternary tin halides

Compound	Shift (mm s^{-1})	Splitting (mm s^{-1})
SnClF	3.73	1.10
Sn_2ClF_3	3.35	1.29
SnBrF	3.59	0.96
Sn_3BrF_5	3.69	1.18
SnIF	3.61	0.76
Sn_2IF_3	3.57	1.34
Sn_2BrCl_3	3.99	0
SnICl	3.71	0.60
SnIBr	3.71	0

ture and Mössbauer data for this compound distinguish it from the formally similar compounds, $\text{Sn}(\text{C}_5\text{H}_5)_2$, $\text{Sn}(\text{C}_5\text{H}_5)\text{Cl}$ and $(\text{Sn}^n\text{Bu}_2)_n$. The cyclopentadienyl compounds have no Sn–Sn bonding and their isomer shift values, which are only just below that for SnCl_2 (4.12 mm s^{-1}), are characteristic of tin(II) compounds with a non-bonding electron pair on each tin atom. In contrast, $(\text{Sn}^n\text{Bu}_2)_n$ is polymeric with strong Sn–Sn interactions in which the formally non-bonding electron pairs on the tin atoms are used in polymerization, and in which the chemical shift and zero quadrupole splitting are indicative of a compound containing both Sn–C and Sn–Sn bonds. The Mössbauer parameters for $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ lie between those for $\text{Sn}(\text{C}_5\text{H}_5)_2$, where there is no Sn–Sn interaction and $(\text{Sn}^n\text{Bu}_2)_n$ where there is a strong interaction. Although the shift for $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ is on the borderline between tin(II) and tin(IV), the value of the quadrupole splitting is not consistent with the formation of Sn–Sn interactions to give a Sn(IV) polymer. The value of the quadrupole splitting is -2.3 mm s^{-1} , the negative sign indicating that there is a deficiency of electrons in the direction of the major component of the field gradient. This in turn means that the z direction of the field is in the direction of an empty or nearly empty p -type orbital and not in the direction of a lone pair, consistent with a tin(II) formulation for the compound. In the chromium pentacarbonyl adduct, $(\text{OC})_5\text{Cr}\cdot\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$, however, the empty p orbital gives rise to a quadrupole splitting of -4.43 mm s^{-1} . The reduction in the size of the quadrupole splitting from 4.43 mm s^{-1} in $(\text{OC})_5\text{Cr}\cdot\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ to 2.31 mm s^{-1} in $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ can only arise because of weak Sn–Sn interactions between neighbouring R_2Sn moieties and indeed crystallographic studies show that molecules are arranged in pairs in the crystal with a very short Sn–Sn distance of only 2.76 Å [76]. This dimeric structure arises from overlap between the lone pair on each tin atom and the empty p orbital of the neighbouring tin atom. On each tin atom there is a direction in which any electron density on the tin must arise from weak interaction with the lone pair on the neighbouring tin atom, and this produces the field gradient.

For tin(II) compounds with the tin in trigonal pyramidal $[\text{SnL}_3]$ sites with Sn–L bonds to the same ligand L, a close connection has been found between the Mössbauer chemical isomer shift and the Sn–L bond distances. For tin compounds with single $[\text{SnF}_3]$ and $[\text{SnO}_3]$ sites, for example, there is an increase in shift with increasing average bond length (Table 3.8), that is, with increasing electrostatic character. Crystals of $\text{Sn}_6\text{O}_6(\text{OMe})_4$ have been shown to consist of two crystallographically non-interacting $[\text{Sn}_6\text{O}_6(\text{OMe})_4]$ units with a central adamantane-like $[\text{Sn}_6\text{O}_4]$ core. The chemical shift value of 2.78 mm s^{-1} is consistent with tin being in the +2 oxidation state and with very short Sn–O bonds ($2.05\text{--}2.08\text{ Å}$) in the $[\text{Sn}_6\text{O}_4]$ skeleton. Those compounds with pyramidal $[\text{SnCl}_3]$ groups and containing only Sn–Cl bonds as nearest and next-nearest neighbours illustrate the relation between Sn–Cl bond length and shift. The similarity of the shift data for monoclinic CsSnCl_3 and

Table 3.8 Mössbauer chemical isomer shift and bond length in tin–oxygen, tin–fluorine and tin–chlorine compounds

Compound	Average bond length (Å)	Shift (mm s ⁻¹)
NH ₄ SnF ₃	2.08	3.25
NaSn ₂ F ₅	2.12	3.32
Sn ₃ F ₈	2.17	3.82
CaSn(CH ₃ CO ₂) ₃	2.14	2.90
KSn(CH ₂ ClCO ₂) ₃	2.16	2.96
KSn(HCO ₂) ₃	2.16	3.08
SnHPO ₃	2.17	3.15
SnSO ₄	2.26	3.95
Co(dpe) ₂ ·Cl·SnCl ₃ · <i>n</i> C ₆ H ₅ Cl	2.43	3.08
Co(dpe) ₂ ·Cl·SnCl ₃	2.44	3.10
CsSnCl ₃ (monoclinic)	2.52	3.64
KCl·KSnCl ₃ ·H ₂ O	2.57	3.70
SnCl ₂	2.74	4.12

[(NH₄)₅CoSO₂C₆H₅][SnCl₃][ClO₄]·H₂O ($\delta = 3.53$ mm s⁻¹, average bond length = 2.52 Å) show that the next-nearest bond in the perchlorate complex, the Sn–O bond of 2.91 Å, produces at the most a very weak perturbation of the tin electron density.

The use of ¹¹⁹Sn Mössbauer spectroscopy, particularly in conjunction with other techniques, has had and will continue to have an important part to play in the interpretation of the bonding characteristics of tin in its +2 oxidation state.

3.2 Tin(IV) chemistry

Tin(IV) oxide is amphoteric and dissolves in aqueous solutions of both acids and alkalis. The predominant tin species present in acid solutions containing complexing anions are the octahedral [SnX₆]²⁻ ions, e.g. with X = F, Cl, Br, I, NCO and NCS. There is also evidence for the formation of mixed-ligand species such as [SnCl₄Br₂]²⁻, [SnF₄(OH)₂]²⁻ and [SnCl₄NO₃]⁻. ¹¹⁹Sn NMR studies have identified [77] all of the possible bromochlorostannates(IV) [SnCl_{*n*}Br_{6-*n*}]²⁻ and most of the chlorofluorostannates(IV), [SnCl_{*n*}F_{6-*n*}]²⁻, including [SnCl₅F]²⁻ and *cis*- and *trans*-[SnCl₄F₂]²⁻, *fac*-[SnCl₃F₃]²⁻, *cis*- and possibly *trans*-[SnCl₂F₄]²⁻ and [SnClF₅]²⁻. Several thiocyanato- and cyano-derivatives, [SnX_{6-*n*}Y_{*n*}]²⁻, where X = Cl or Br and Y = CN or NCS, have also been identified in aqueous solution [78].

The main species present in alkaline solutions containing an excess of hydroxide ion is [Sn(OH)₆]²⁻ but in less basic solutions dehydration may occur to give ions such as [SnO₃]²⁻. SnS₂ is soluble in aqueous alkaline solutions containing sulphide ions because of the formation of [SnS₃]²⁻. Some

tin(IV) compounds [e.g. SnCl_4 and $\text{Sn}(\text{SO}_4)_2$] are soluble in water but are subject to hydrolysis and, in fact, in the absence of strong complexing anions, all aqueous solutions of Sn(IV) tend to hydrolyse to give a precipitate of hydrous tin(IV) oxide.

A number of tin(IV) materials are soluble in non-aqueous solvents. Tin(IV) chloride and bromide are soluble in glycol, acetone, pyridine, benzene, dimethylsulphoxide and many other organic solvents, and the complex ions $[\text{SnCl}_5]^-$ and $[\text{SnBr}_5]^-$ can be obtained from solutions of the halides in dichloroethane. Tin(IV) iodide is soluble in a wide range of non-aqueous solvents including carbon tetrachloride, chloroform, benzene, heptane, diethyl ether, toluene and carbon disulphide. A number of complex tin(IV) species have been identified in non-aqueous solutions, including $[\text{Sn}(\text{NH}_2)_6]^{2-}$ in liquid ammonia, $[\text{Sn}(\text{HSO}_4)_6]^{2-}$ in 100% H_2SO_4 and $\text{SnX}_4 \cdot 2$ ligand for many solutions of tin(IV) halides in donor solvents which can act as ligands. Tin(IV) chloride in liquid N_2O_4 gives the ionic salt $\text{NO}^+[\text{SnCl}_4(\text{NO}_3)]^-$. Both tin(IV) chloride and bromide can, because of their Lewis acid properties, act as non-aqueous solvents.

Tin(IV) carboxylates are not well known, although $\text{Sn}(\text{CH}_3\text{CO}_2)_4$ can be prepared from SnI_4 and acetic anhydride or from tetravinyltin in anhydrous acetic acid. The cleavage of tetravinyltin by carboxylic acids is a general reaction and the compounds $\text{Sn}(\text{RCO}_2)_2$ ($\text{R} = \text{H}$, C_2H_5 , iso- C_4H_9 , n - C_4H_9 and n - $\text{C}_{11}\text{H}_{23}$) have been prepared. Tin(IV) nitrate, $\text{Sn}(\text{NO}_3)_4$, is prepared by the action of N_2O_5 with SnCl_4 followed by vacuum sublimation at 40°C . It reacts readily with aliphatic hydrocarbons and vigorously with diethyl ether, probably because of the formation of a $\text{NO}_3\cdot$ radical. It also forms the adduct, $\text{Sn}(\text{NO}_3)_4 \cdot 2\text{py}$, in which the nitrate groups are unidentate. The action of hydrous tin(IV) oxide on phosphoric acid results in the precipitation of a gel of approximate formula $\text{Sn}(\text{P}_2\text{O}_5)_{0.6}(\text{H}_2\text{O})_{4.9}$. This is probably a basic salt and is known to act as an ion exchange material. Reaction of $\text{K}_4\text{P}_2\text{O}_7$ with SnO_2 gives the pyrophosphate SnP_2O_7 , and the mixed phosphate $\text{KSn}_2(\text{PO}_4)_3$ has also been reported. Tin(IV) hypophosphite, $\text{Sn}(\text{H}_2\text{PO}_2)_4$, is obtained as a white crystalline solid by the oxidation of solutions of tin(II) hypophosphite. The mixed salt $\text{Sn}(\text{H}_2\text{PO}_2)_4 \cdot \text{SnCl}_4$ has also been prepared. $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been obtained as deliquescent white crystals from Sn(IV) solutions. Anhydrous $\text{Sn}(\text{SO}_4)_2$ is said to exist, and the mixed sulphates $\text{K}_2\text{Sn}(\text{SO}_4)_3$ and $\text{CaSn}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ have been prepared.

3.2.1 Structure and bonding in tin(IV) chemistry

The structural chemistry of inorganic tin(IV) derivatives is relatively simple, being for the most part based on tetrahedral coordination in molecular compounds and on octahedral geometry in compounds with more ionic bonding and in most of its complexes. There are, however, examples of five- seven- and eight-coordination.

The halides SnX_4 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) are tetrahedral molecules in the vapour phase. Solid SnBr_4 and SnI_4 have structures consisting of hexagonally close-packed halogen atoms with tin occupying one-eighth of the tetrahedral holes. In both, the tin atoms have a distorted tetrahedral environment, the distortion being greatest for SnBr_4 . Stannane, SnH_4 , is also tetrahedral, and reacts with sodium in liquid ammonia to give NaSnH_3 and Na_2SnH_2 . Halostannanes such as ClSnH_3 are also known but are stable only at lower temperatures. Tetrahedral tin sites are also found in $\text{Sn}(\text{NCPh}_2)_4$, $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{SnBr}$, K_4SnO_4 and in a range of sulphide derivatives including $\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})_2$, K_2SnS_3 , Na_4SnS_4 , M_2SnS_4 , Cu_2MSnS_4 ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$), Eu_2SnS_5 , $\text{Na}_4\text{Sn}_2\text{S}_6$, $\text{Na}_6\text{Sn}_2\text{S}_7$, $\text{Eu}_3\text{Sn}_2\text{S}_7$, BaCdSnS_4 and $\text{M}_3\text{Sn}_2\text{S}_7$ ($\text{M}=\text{Ca}, \text{Ba}$). Some of these compounds, for example Na_4SnS_4 , contain discrete $[\text{SnS}_4]^{4-}$ tetrahedra, while other compounds are said to contain discrete condensed anions such as $[\text{Sn}_2\text{S}_6]^{4-}$ (in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$) and $[\text{Sn}_2\text{S}_7]^{4-}$ (in $\text{Na}_6\text{Sn}_2\text{S}_7$). Two tetrahedral tin(IV) sites have also been found [79] in Eu_2SnS_5 . Both sites are distorted, one having bond lengths in the range 2.37–3.50 Å and the other in the range 2.32–3.01 Å.

In most of its solid state compounds tin is in a six-coordinated site. It has octahedral symmetry in SnO_2 which has the rutile structure, and in SnS_2 which crystallizes in the CdI_2 lattice. Tin forms a wide range of stannates(IV) in which it is generally to be found in six-coordination. Typical stannates(IV) include BaSnO_3 , K_2SnO_3 , $\text{Na}_2\text{Sn}_2\text{O}_5$, $\text{Ca}_2\text{Sn}_2\text{O}_7$, Ca_2SnO_4 and Co_2SnO_4 . The amount of distortion of tin sites can vary from negligible in SnO_2 to considerable in compounds such as CaSnSiO_5 , in which the tin is in a tetragonally distorted site with two short axial bonds of 1.947 Å and four longer equatorial bonds of about 2.09 Å. Tin is also in octahedral environments in the sulphides Sn_2S_3 , Cu_2SnS_4 and $\text{Cu}_2\text{FeSnS}_4$.

Solid tin(IV) fluoride, SnF_4 , has a distorted octahedral environment with two short and, four long Sn–F bonds and is isostructural with PbF_4 . Most of the solid derivatives of the $[\text{SnX}_6]^{2-}$ ions ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) have tin in regular six coordination, and the alkali metal salts have the K_2PtCl_6 structure. The reaction of tetrafulvalene (TTF) with SnCl_4 gives $[\text{tff}][\text{SnCl}_6]$ which contains [80] the $[\text{SnCl}_6]^{2-}$ anion in which Sn–Cl bond lengths (2.437–2.438 Å) are longer than those normally found in this ion. The $[\text{SnBr}_6]^{2-}$ ion in $[\text{NH}_2\text{Me}_2][\text{SnBr}_6]$ has [81] two bonds of 2.609 Å and four of 2.601 Å in contrast to $[\text{Hpy}]_2[\text{SnBr}_6]$ [82] which has three distinct Sn–Br distances, 2.63, 2.58 and 2.56 Å. BaSnF_6 is said to have a regular and Na_2SnF_6 a distorted octahedral environment for tin. Six-coordinated tin environments are also present in K_3HSnF_8 and in most hexahydroxystannates(IV) (e.g. $\text{MSn}(\text{OH})_6$, $\text{M}=\text{Ca}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}$).

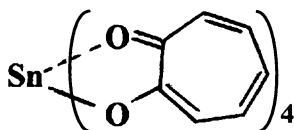
Tin(IV) forms a wide range of six-coordinated complexes with chelating ligands such as EDTA, acetylacetone, salicylaldehyde, dithiols and 8-hydroxyquinoline, for example bis(toluen-3,4-dithiol)Sn(IV), tetrakis(8-hydroxyquinolate)Sn(IV), SnY_2X_2 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$; $\text{Y}=\text{8-tetrakis(8-hydroxy-$

quinolate), salicylaldehyde, acetylacetonate). Tin(IV) chloride has been shown to form 1:1 and 2:1 addition complexes of the type $\text{SnCl}_4[\text{NiL}]\cdot\text{H}_2\text{O}$, and $2\text{SnCl}_4[\text{NiL}]\cdot\text{H}_2\text{O}$ with $[\text{NiL}]\cdot\text{H}_2\text{O}$ complexes where, for example, L is bis(3-methoxysalicylidene)ethylenediamine [83]. Six-coordinated tin(IV) complexes of the type SnL_2X_2 have also been prepared where HL is a monobasic chelating ligand and $\text{X} = \text{Cl}, \text{Br}$ or I [84]. The crystal structures of $\text{SnL}_2\text{Cl}_2\cdot\text{CH}_3\text{Cl}$, L=maltol, and SnL_2Cl_2 , L=tropolone, show that the tin atoms in both complexes have bonds to two chlorine atoms at approximately 2.36 Å and to four oxygens from the chelating groups with bond distances in the range 2.04–2.15 Å. These complexes can exist as five geometrical isomers and the interrelationships between them have been studied by variable temperature ^{119}Sn NMR spectroscopy. Geometrical isomerism was found to be normally slow on the NMR timescale and in some cases slow- and fast-exchange spectra were obtained in the variable temperature study.

The tin(IV) halides and many other tin(IV) materials act as acceptors and form complexes with neutral donor ligands [85]. Six-coordinated tin(IV) complexes of the type $\text{SnX}_4\cdot 2\text{L}$ are known in which ligand atoms can either be in *cis* or *trans* positions. The *cis*-adducts are usually distorted in such a way that the SnX_4 residue is very similar to the original tetrahedral SnX_4 and most $\text{SnX}_4\cdot 2\text{ligand}$ complexes appear to have this structure. The compounds $\text{SnCl}_4\cdot 2\text{CH}_3\text{CN}$, $\text{SnCl}_4\cdot 2\text{POCl}_3$, $\text{SnCl}_4\cdot 2\text{SeOCl}_2$, $\text{SnBr}_4\cdot 2\text{oxH}$ (oxH=8-hydroxyquinoline) are known to be *cis*. The ligands are, however, thought to be in *trans* positions in $\text{SnBr}_4\cdot 2\text{salicylaldehyde}$, $\text{SnCl}_4\cdot 2\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{SnCl}_4\cdot 2\text{As}(\text{C}_2\text{H}_5)_3$. Di-ligand complexes of tin(IV) halides with a very large variety of donor molecules are known including those with N-donors (pyridine, NH_3 , aniline, nitriles and many amines), P-donors (triethyl- and triphenyl-phosphines and PH_3), O-donors (carboxylic acids, aldehydes, ketones, alcohols, esters, H_2O , phosphine oxides and sulphoxides) and S-donors (thiourea and alkyl sulphides). Complexes with As- and Sb-donors are also known. A number of 1:1 complexes have been reported including $\text{SnBr}_4\cdot \text{N}(\text{CH}_3)_3$, $\text{SnCl}_4\cdot \text{P}(\text{C}_6\text{H}_5)_3$, $\text{SnF}_4\cdot \text{thf}$ and $\text{SnCl}_4\cdot \text{oxH}$. Among the complexes found with other tin(IV) compounds are $\text{Sn}(\text{NO}_3)_4\cdot 2\text{py}$, $\text{Sn}(\text{NO}_3)_4\cdot 6\text{N}(\text{C}_2\text{H}_5)_3$, and bis(ethane-1,2-dithiolato) $\text{Sn}(\text{IV})\cdot 2\text{L}$ (L=pyridine, dimethylsulphoxide).

In addition to the more common four- and six-coordination found for tin in its +4 oxidation state, there are some compounds in which the tin environments are more easily described in terms of five-, seven- or eight-coordination. The $[\text{SnCl}_5]^-$ ion in its 3-chloro-1,2,3,4-tetraphenylcyclobutenium salt has a five-coordinated trigonal bipyramidal structure with equatorial bond lengths and angles of 2.30–2.40 Å and 114–126°, axial bond lengths of 2.37–2.39 Å and equatorial-axial bond angles of 90°. Five-coordination has also been reported for tin(IV) in SnTa_2O_7 , K_2SnO_3 and for one site in $\text{Eu}_3\text{Sn}_3\text{S}_{12}$. Seven-coordination has been ascribed to tin in a number of compounds including $\text{Sn}(\text{edta})\cdot\text{H}_2\text{O}$, $\text{K}_6\text{Sn}_2[\text{C}_2\text{O}_4]_7\cdot 4\text{H}_2\text{O}$ and

(Me₄N)[Sn(OCOCH₃)₅]. The eight-coordinated tin structures found for tin in Sn(CH₃CO₂)₄ and Sn(NO₃)₄ are illustrated in Chapter 2 [structure (60)]. Tin has also been shown to be eight-coordinated in the crystal structure of the tropolonate [86].



3.2.2 Mössbauer spectroscopy of tin(IV) compounds

The ¹¹⁹Sn Mössbauer chemical shifts (δ) for most tin(IV) materials follow the trends expected in that they increase as the covalent character of the bonding increases [92]. For example, shifts of the tetrahalides are more positive (Table 3.9) with increasing covalent character of the Sn–X bond, that is with the trend away from the 4d¹⁰, Sn⁴⁺ ion. Similar relationships have been found for all halogeno-tin compounds and there is a linear relationship between δ for the [SnX₄Y₂]^{2–} complexes (X, Y = Cl, Br, I) and the sum of the electronegativities

Table 3.9 Mössbauer parameters for tin(IV) compounds

Compound	Shift (mm s ^{–1})	Splitting (mm s ^{–1})
SnF ₄	–0.47	1.16
SnCl ₄	0.85	0
SnBr ₄	1.15	0
SnI ₄	1.55	0
K ₂ SnF ₆	–0.59	0
K ₂ SnCl ₆	0.45	0
K ₂ SnBr ₆	0.75	0
K ₂ SnI ₆	1.30	0
SnCl ₄ ·2NMe ₃	0.54	0
SnCl ₄ ·2MeCN	0.43	0.70
SnBr ₄ (oxinH) ₂	0.65	0
SnBr ₄ (salH) ₂	0.73	1.22
Ph ₂ SnCl ₂	1.34	2.89
Me ₃ SnCl	1.43	3.32
SnZn ₂ O ₄	0.10	0.75
SnO ₂	0	0
Cu ₂ FeSnS ₄	1.48	0
<i>trans</i> -SnCl ₄ (tht) ₂	0.72	0.35
<i>cis</i> -SnCl ₄ (tht) ₂	0.70	0.24
<i>trans</i> -SnCl ₄ (dmsO) ₂	0.41	0.57
<i>cis</i> -SnCl ₄ (dmsO) ₂	0.40	0.41
<i>trans</i> -SnCl ₄ (dmf) ₂	0.38	0.73
<i>cis</i> -SnCl ₄ (dmf) ₂	0.39	0.53
<i>trans</i> -SnBr ₄ (dmf) ₂	0.66	0.83
<i>cis</i> -SnBr ₄ (dmf) ₂	0.66	0.44
<i>trans</i> -SnCl ₄ (dma) ₂	0.38	0.78
<i>cis</i> -SnCl ₄ (dma) ₂	0.38	0.45

of the halogens bonded to tin. The increase in the coordination number from four in the tetrahalides to six in complexes also represents an increase in the electrostatic character of the bonds to tin(IV), and is reflected in a decrease in the shift for the tin(IV) halide complexes with neutral donor ligands, (SnCl_4 , K_2SnCl_6 and $\text{SnCl}_4 \cdot 2\text{NMe}_3$ in Table 3.9). The shift becomes greater with increasing donor ligand electronegativity. For example, the shifts for $\text{SnCl}_4 \cdot 2\text{L}$ are 0.22, 0.33, 0.46 and 0.71 mm s^{-1} , respectively, for $\text{L} = (\text{C}_6\text{H}_5)_3\text{PO}$, $(\text{CH}_3)_2\text{SO}$, py and $(\text{C}_6\text{H}_5)_3\text{P}$. Very few inorganic tin(IV) compounds show a quadrupole splitting (Δ) of the resonance line, which indicates little imbalance in the p - or d -electron distribution around tin. Zero splittings are expected for compounds with high symmetry environments (e.g. SnCl_4 and BaSnO_3), but deviations from ideal geometry do not in themselves give rise to a p -electron imbalance reflected in a quadrupole splitting (for example $\text{SnCl}_4 \cdot 2\text{NMe}_3$, $\text{SnCl}_2(\text{oxine})_2$ and SnCl_2Br_2 all have zero splitting values). Quadrupole splittings only arise when the bond characteristics of one type of tin-element interaction present is significantly different from the others. The presence of two short and four long bonds in SnF_4 does, for example, produce an electronic imbalance and gives a splitting of 1.80 mm s^{-1} . A few tin(IV) halide complexes with neutral donor molecules also have tin–ligand bonds sufficiently different from Sn-X to produce a field gradient [e.g. *trans*- $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}$ (0.97 mm s^{-1}); *cis*- $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ (0.91 mm s^{-1}) and *cis*- $\text{SnCl}_4 \cdot 2\text{Cl}_3\text{PO}$ (1.12 mm s^{-1}) all have resolvable splittings]. The splitting in the nitrile adduct is due to the presence of very weak Sn-N bonds. Since the splitting for a *trans* complex should be twice that of a corresponding *cis* complex, it has been possible to distinguish between *cis*- $\text{SnBr}_4 \cdot 2(8\text{-hydroxyquinoline})$ ($\Delta = 0$) and $\text{SnBr}_4 \cdot 2(\text{salicylaldehyde})$ ($\Delta = 1.11 \text{ mm s}^{-1}$). The data [93] for some *cis*- and *trans*- SnCl_4 complexes are given in Table 3.9. The five-coordinated species $[\text{SnCl}_5]^-$ is of sufficiently low symmetry to show a splitting of 0.63 mm s^{-1} . Although no resolvable quadrupole splitting is found for mixed halides $[\text{SnX}_n\text{Y}_{6-n}]^{2-}$, the Mössbauer spectrum for the mixed hexahalogenostannates(IV) found in glassy aqueous mixed halide solutions do have broader resonance lines than the single halide $[\text{SnX}_6]^{2-}$ species [94].

Variable temperature Mössbauer studies have been used to provide information on the nature of association of tin species in solids. The complexes $\text{SnCl}_4 \cdot 2\text{L}$ ($\text{L} = \text{detu}$ and dmu) are, for example, non-interacting discrete molecules [95] while LiFeSnO_4 , in both its high and low temperature forms, has a three-dimensional lattice but with a considerable amount of covalency in the Sn-O bond [96]. Mössbauer spectroscopy has also been used to show that tin occupies copper sites in tin-doped copper-containing superconductor phases [97].

3.2.3 Solid state chemistry of tin(IV) compounds

Perhaps the most important recent development in tin(IV) chemistry has

been the increase in studies of the solid state properties of tin(IV) compounds. Tin(IV) oxide, stannates(IV), and mixed-metal oxide phases containing tin(IV) have interesting physical properties as bulk solids and as thin films [98]. Tin(IV) oxide itself, for example, is an oxygen-deficient lattice and an *n*-type semiconductor with a band gap of 3.7 eV. The mixed-metal oxide phases antimony–tin oxide and indium–tin oxide have good electrical conductivity leading to commercial applications. Other tin(IV) oxide phases which have been studied include the Sn(IV)-doped $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ perovskite superconductors, SnO_2 –Eu phosphors, indium–tin oxide piezoelectric ceramics, $\text{K}_x(\text{In}_x\text{Sn}_{1-x})\text{O}_2$ ionic conductors and $\text{Bi}_2\text{SrCa}(\text{Cu},\text{Sn})_2\text{O}_{8-y}$ and $\text{YBa}_2\text{Cu}_{3-x}\text{Sn}_x\text{O}_{7-y}$ superconductors.

Tin(IV) compounds have been used as intercalate host lattices [99, 100]. The chlorotin arsenate and phosphate phases $[\text{SnCl}(\text{OH})\text{XO}_4] \cdot 2\text{H}_2\text{O}$ ($\text{X}=\text{P}, \text{As}$), for example, will intercalate short chain fatty acids and some amines.

Another area of current interest in solid state tin(IV) chemistry is concerned with complexes of crown ethers. Compounds like $\text{SnX}_4\text{L} \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4\text{L} \cdot 4\text{H}_2\text{O} \cdot n\text{CHCl}_3$, where L is a crown ether, have been synthesized [101]. The structure of $\text{Sn}(\text{OH}_2)_2\text{Cl}_4 \cdot 18\text{-crown-6} \cdot 2\text{H}_2\text{O} \cdot \text{CHCl}_3$ contains octahedral $[\text{Sn}(\text{OH}_2)_2\text{Cl}_4]$ units with the water molecules lying *cis* to each other, and involved in an extensive hydrogen bonding scheme. The crown ether complexes of 2SnCl_4 ·dibenzo-24-crown-8 [102] and SnCl_4 ·18-crown-6·4 H_2O have been reported, and the structure of the latter determined [103]. The crystal structure of the complex of 15-crown-5 (1,4,7,10,13-pentaoxocyclopentadecane) with diaquatetrachlorotin(IV) at 120 K has also been determined [104], and consists of octahedral $[\text{SnCl}_4(\text{H}_2\text{O})_2]$ units linked by bifurcated hydrogen bonds from the water molecules to the 15-crown-5 molecules. The formation of the complex does, however, result in an unusual *trans* distribution of water molecules with Sn–O distances of 2.11 and 2.13 Å and Sn–Cl distances of 2.36–2.39 Å. The crown thioether chemistry of tin(IV) has also been studied recently [105].

3.3 Mixed-valence tin compounds

A number of mixed-valence compounds which contain both bivalent and tetravalent tin have been studied. The best known is Sn_2S_3 , which can be prepared as acicular crystals by heating a powdered mixture of the appropriate proportions of tin and sulphur to 993 K in a sealed tube. Sn_2S_3 contains [106] octahedrally coordinated tin(IV) with Sn–S distances of 2.459–2.604 Å and bond angles of 86.4–91.1°. The tin(II) site has the typical trigonal pyramidal arrangement of atoms around the tin, with Sn–S bond lengths of 2.645–2.765 Å. The compound is a semiconductor and its electrical properties have been studied [107, 108]. The mixed-valence sulphide $\text{Sn}^{\text{II}}_4\text{Sb}^{\text{III}}\text{Sn}^{\text{IV}}\text{S}_9$,

consists of a cube face distribution of $[\text{Sn}^{\text{IV}}\text{S}_6]$ octahedra linked through $[(\text{Sn}^{\text{II}}, \text{Sb}^{\text{III}})\text{S}_8]$ dodecahedra which are lone-pair distorted [109].

The oxidation of SnF_2 in HF with O_2 , F_2 or SO_2 yields the insoluble mixed oxidation state compound Sn_3F_8 , whose structure shows *trans*-fluorine-bridged $[\text{Sn}^{\text{IV}}\text{F}_6]$ units linked to polymeric $[\text{Sn}^{\text{II}}\text{F}]_\infty$ chains [110]. The tin(IV) atoms are octahedrally coordinated by fluorines. The marginally longer bonds are to the *trans*-fluorines which also interact with the tin(II) atoms. The tin(II) atoms are not only linked to tin(IV) by bridging fluorines, but also to one another by the other fluorine atoms. This latter interaction produces nearly coplanar zigzag $-\text{Sn}-\text{F}-\text{Sn}-\text{F}-$ chains running through the structure. The overall structure may be represented by the formula $(\text{SnF})_2\text{SnF}_6$, the tin(II) sites being pyramidal with Sn–F bonds of 2.10, 2.17 and 2.25 Å and a next-nearest contact of 2.55 Å. The structure of $(\text{NH}_4)_3\text{Sn}_3\text{F}_{11}$ has also been determined [111], and it has been suggested that the material is best formulated as $(\text{NH}_4)_3(\text{Sn}_2\text{F}_5)(\text{SnF}_6)$. Two types of $[\text{SnF}_6]^{2-}$ octahedra are present in the lattice, one of which is much more distorted than the other. The $[\text{Sn}_2\text{F}_5]^-$ species have terminal Sn–F bonds of 2.05 Å and a bridging bond of about 2.13 Å. It is significant that this compound is an ionic conductor and that there is no evidence for any electronic conduction arising from the presence of both tin(II) and tin(IV) species in the lattice. Mixed-valence fluorotin carboxylates have been prepared by reacting SnF_2 with $\text{Sn}(\text{RCO}_2)_4$. The crystalline compound isolated from SnF_2 – $\text{Sn}(\text{CF}_3\text{CO}_2)_4$ solutions has been shown [112] to be $\text{Sn}^{\text{II}}_2\text{Sn}^{\text{IV}}_2\text{F}_4(\text{CH}_3\text{CO}_2)_8 \cdot 2\text{CF}_3\text{CO}_2\text{H}$. Its structure contains two only slightly different *cis*-fluorine-bridged tin(IV) environments, consistent with the single line found in the Mössbauer spectrum of the compound ($\delta = -0.16 \text{ mm s}^{-1}$). The lattice also contains two lone-pair distorted tin(II) sites which exhibit a single Mössbauer resonance line ($\delta = 4.13 \text{ mm s}^{-1}$, $\Delta = 0.84 \text{ mm s}^{-1}$). The total structure comprises two independent centrosymmetric units, each unit consisting of an eight-membered ring with a unit $-\text{Sn}^{\text{II}}-\text{F}-\text{Sn}^{\text{IV}}-\text{F}-$ arrangement. Adjacent tin(II) and tin(IV) atoms in the units are also bridged by either one or two trifluoroacetate groups. There are also unidentate trifluoroacetate groups and acid molecules coordinated to the tin atoms. Eight trifluoroacetate groups are associated with each tetramer, and the two trifluoroacetic acid molecules are associated with only one of the units and coordinated to two tin(II) atoms.

The mixed-metal oxides $\text{Sn}^{\text{II}}_{2-x}(\text{M}^{\text{V}}_{2-y}\text{Sn}^{\text{IV}}_y)\text{O}_{7-x-y}$ ($\text{M} = \text{Nb}, \text{Ta}$) are examples of tin(II)–tin(IV) compounds in which the tin(II) environment is lone-pair distorted and similar to that found in tin(II) sulphate [113]. It has also been claimed [114] that octahedral tin(IV) and pyramidal tin(II) sites are also present in Sn_2O_3 . The crystal structure of the mixed-valence carboxylate $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{OCOC}_6\text{H}_4\text{NO}_2-2)_4\text{O} \cdot \text{thf}]_2$ has been determined [115]. The structure (Figure 3.9) consists of independent tetranuclear clusters containing two tin(II) and two tin(IV) atoms. The main feature of the cluster is a lozenge-shaped four-membered $[\text{Sn}^{\text{IV}}_2\text{O}_2]$ ring, with octahedral coordination of the tin

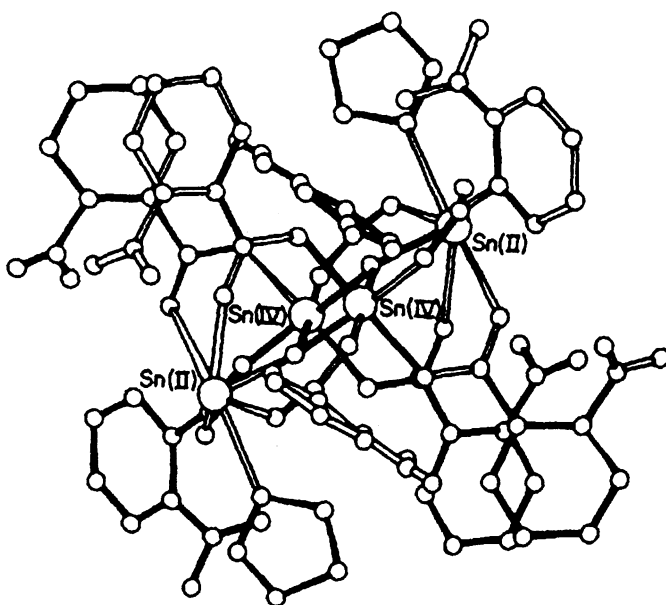


Figure 3.9 Tetranuclear clusters in $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}_2\text{C}_6\text{H}_4\text{NO}_2-2)_4\text{O}\cdot\text{thf}]_2$. (Reproduced by permission from Ref. 115.)

being completed by oxygen atoms from four *o*-nitrobenzoate groups which form bridges between the tin atoms in the two oxidation states. The tin(IV)-oxygen bond distances are in the range 2.047–2.067 Å and the geometry at tin(II) is a distorted pyramid with oxygen atoms from four bridging carboxylate groups and THF occupying equatorial positions at bond distances in the range 2.41–2.66 Å but with a relatively short (2.11 Å) Sn(II)–O distance in an apical position. The variable temperature Mössbauer data for this compound show that the tin(IV) atoms are more strongly held in the lattice than the tin(II) atoms.

The most significant feature of the mixed-valence compounds of tin is that, for compounds in which the tin is bonded to oxygen or fluorine atoms, there is no evidence for any inter-valence transfer adsorption or of electrical properties arising from hopping mechanisms. Electrical conductivity only arises in Sn_2S_3 where the sulphur atoms have vacant *d*-orbitals, and for which direct population of solid state bands, as in the case of CsSnBr_3 and similar compounds (section 3.1.3), is a more likely explanation for the optical and electrical properties of the compound than inter-valence electron hopping. The ^{119}Sn Mössbauer data for the mixed-valence compound from the 8:1:1 system $\text{In}_2\text{F}_3\text{--SnS--SnS}_2$ have been recorded over the range 80–300 K [116]. The structure is based on the cubic $\alpha\text{-In}_2\text{S}_3$ spinel lattice with vacancies and has the formula, $[\text{In}, \square]_8[\text{In}, \text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}]_{18}\text{S}_{32}$ and the recoilless fraction of the Sn^{IV} and Sn^{II} sites were found to be 0.71 and 0.61, respectively.

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4 Formation and cleavage of the tin–carbon bond

J.L. WARDELL

4.1 Preparation of tin(IV)-carbon bonds

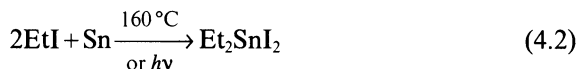
4.1.1 General methods

Direct synthesis [1–3]. The direct reaction of tin (as foil, powder or alloy) with organic halides has been widely used in the laboratory as a route to organotin species (eqn 4.1). Catalysts and/or promoters are required for all but the most reactive alkyl halides. The directness of the method has clear attractions as an industrial process, but so far only limited use has been made



of it. One example of the direct reaction [4], as a manufacturing process, is the synthesis of Me_2SnCl_2 , from tin foil and MeCl with $\text{Ph}_3\text{MeP}^+\text{Br}^-$ as catalyst and KI as promoter at $180\text{--}190^\circ\text{C}$. The direct synthesis in industry is probably limited because the predominant products are usually diorganotin compounds. The report [5] by Holland of the direct and economic formation of triorganotin compounds from tin and alkyl halides in high yields may well change this situation. The Holland process involves addition of the alkyl halide to tin powder dispersed in a molten quaternary halide, such as R_4NX , at $120\text{--}140^\circ\text{C}$, which rapidly produces the trialkyltin halide and R_4NSnX_3 . Tin, the quaternary halide and halide can be recovered from R_4NSnX_3 by electrochemical means and can all be reused. The alkylation of tin occurs in a stepwise manner and it is possible to stop the process at the mono- or diorganotin stage.

The initial report of a direct method was by Frankland in 1849 (eqn 4.2). Subsequently, various allyl-, benzyl- and alkyltin halides have been obtained by direct synthesis, e.g. functionally substituted alkyltin compounds have been obtained [1, 2, 6] from $\text{YCO}(\text{CH}_2)_n\text{X}$ ($n = 1, 2$; $\text{X} = \text{halide}$, $\text{Y} = \text{R}_2\text{N}$, RO or R), $\text{NCCH}_2\text{CH}_2\text{X}$ and $\text{RO}(\text{CH}_2)_3\text{I}$, as well as from halo-succinates and malonate [7–9]. The reactivity of the alkyl halides is in the sequence $\text{RI} > \text{RBr} > \text{RCl}$ and $\text{MeX} > \text{EtX} > \text{PrX}$. Particularly reactive halides are benzyl halides; catalysts are not required in the PhCH_2Cl –tin reactions in H_2O or in toluene which produce $(\text{PhCH}_2)_3\text{SnCl}$ or $(\text{PhCH}_2)_2\text{SnCl}_2$, respectively [10–12].



Various catalysts/promoters have been employed for less reactive halides, including other metals (sodium, magnesium, zinc or copper) [1, 2], Lewis bases (amines, alcohols or ethers), halides (iodides, quaternary ammonium halides or cuprous halides), and triorganophosphines or -stibines. While in the main, diorganotin species predominate, the use of certain catalysts can lead to higher alkylations, e.g. tin-sodium alloys provide tri- and even tetraalkyltins.

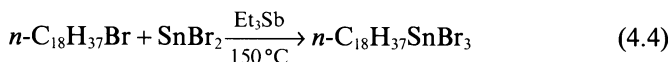
Electrochemical methods can be mentioned; oxidation of anionic tin in a solution of RX in benzene provides R_2SnX_2 [13–16]. Other electrochemical syntheses have been reported using a tin cathode, e.g. as in the preparation of Me_4Sn (from MeI) [15] and $(NCCH_2CH_2)_4Sn$ [18] from $NCCH_2CH_2I$.

The so-called diestertin dichlorides, $Cl_2Sn(CH_2CH_2CO_2R)_2$, have been obtained [19,20] by reaction of powdered tin, hydrogen chloride and an α,β -unsaturated carbonyl species, e.g. acrylic esters in ether (eqn 4.3):



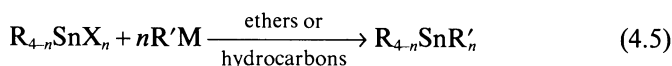
Di- β -keto- and -amido- (as well as -cyano)alkyltin dihalides have also been obtained. It has been suggested that probable intermediates are $H^+SnCl_3 \cdot Et_2O$ or $(H^+)_2 \cdot SnCl_4^2- \cdot 2Et_2O$.

Tin(II) halides have also been used [1,2] in direct synthesis with alkyl halides to give R_4SnX_2 . While similar catalysts/promoters have been employed for tin(II) halides as used for tin, particularly effective are R_3Sb [21, 22], e.g. for use with $C_nH_{2n+1}X$ and $X(CH_2)_nX$, (eqn 4.4). The reactivity sequences established [1, 14] for SnX_2 and for RX are $X = I > Br > Cl$, while for C_nH_{2n+1} , the reactivity decreased with increasing n .



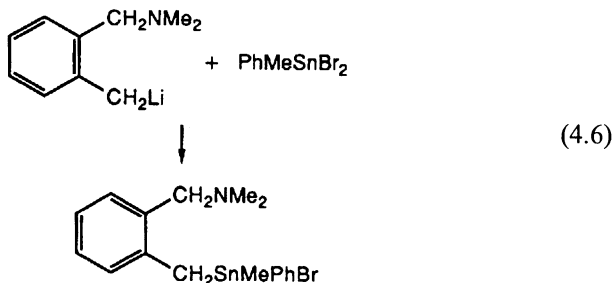
Estertin trichlorides, $Cl_3SnCH_2CH_2CO_2R$, are available [19,20] from tin(II) chloride, hydrogen chloride and acrylic esters, $CH_2=CHCO_2R$.

From tin halides and organic derivatives of other metals [17, 23]. Reactions of organotin halides and tin(IV) tetrahalides with organic derivatives of electro-positive elements are arguably the most important routes to compounds with new tin-carbon bonds:

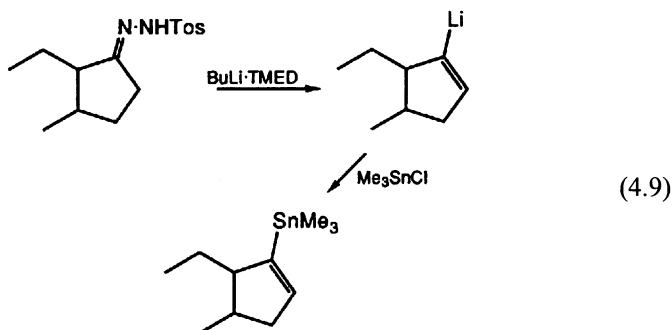
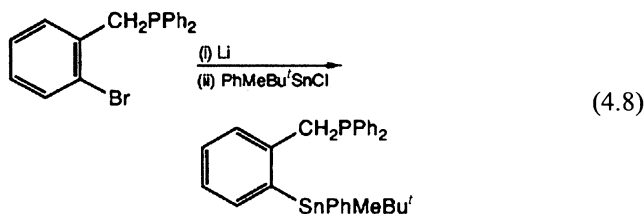


The metals, M, most frequently employed in the laboratory are magnesium and lithium, with sodium, zinc and aluminium playing more limited roles. Usually tetraorganotin compounds are the target products, particularly as it is difficult to stop the alkylation at a predetermined stage. However, in certain cases this has been achieved [24, 25], e.g. eqn 4.6. There is a greater

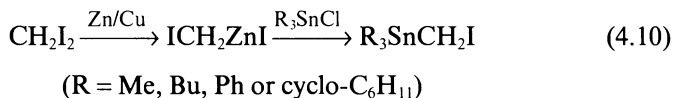
probability of partial alkylation occurring with Grignard reagents in Et_2O than with the corresponding lithium species in THF as well as with bulky organic units, e.g. cyclohexyl groups [25, 26].



This method is clearly limited by the availability and stability of $\text{R}'\text{M}$ as well as to functional groups inert to $\text{R}'\text{M}$ under the chosen reaction conditions. Organolithium compounds are particularly useful. A wide range of substituted alkyl-, alkenyl-, alkynyl- and aryllithium species is obtainable from lithium, simple organolithium reagents (e.g. BuLi , Bu^iLi , Bu^tLi , MeLi , etc.) or $\text{R}'_2\text{NLi}$, by such reactions as lithiations of hydrocarbons or lithium-halide exchanges with organic halides [27]. Use of low temperatures and masked/protected groups may, however, be necessary to preserve certain functional groups. Some examples are given [28–30] in eqns 4.7–4.9.



Transmetallations using organozinc compounds have found specific use in the formation of iodomethyltin compounds [31] (eqn 4.10).



Reformatsky reagents have also been employed [32], e.g. eqn 4.11.



Tin-oxygen and tin-sulphur bonded compounds may be used as alternatives to tin halides [23]. Reactions of tin sulphides with organomercurials have also been used [33, 34], e.g. eqn 4.12.



where R = H or COR²; R² = OEt, Me.

From triorganostannyl-alkali metal, -magnesium and -copper compounds [23, 35, 36]. Triorganostannyl-metal compounds, stannylanionoids, R₃SnM (M = Li, Na, K, MgX or Cu) are finding extensive use for the preparations of mixed compounds, R₃SnR¹ (R¹ = simple or substituted alkyl, vinyl, allyl, aryl, etc.). Reactions occur with organic halides and tosylates, aldehydes, ketones, β-enones and alkynes as well as with small ring compounds such as epoxides, oxetanes and their sulphur analogues.

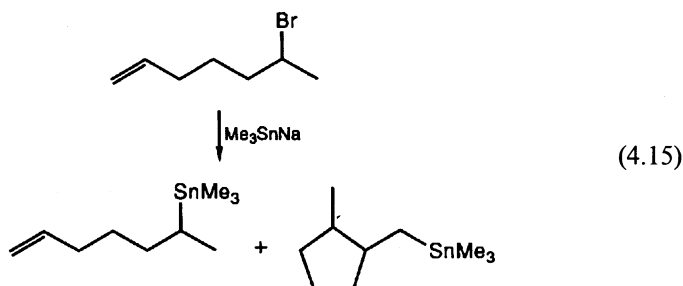
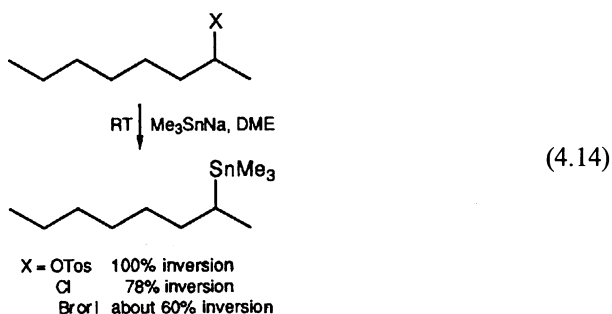
R₃SnM (M = alkali metal or MgX) can be obtained [23, 35, 36] from (1) R₃SnX (X = halides) and M (Li, Na, Mg) or ArH[−], M⁺ (e.g. ArH = naphthalene or phenanthrene; M = Li, Na or K) in ethers (Et₂O, THF, DME, tetraglyme, etc.) or less frequently in liquid ammonia; (2) R₃SnSnR₃ and M (M = Li, Na or K) in ethers, RLi in HMPA or R₂NLi; or (3) R₃SnH and MH (M = Na or K), Bu'MgX (for R = Bu), R₂NLi or R₂NM-LiOBu' (M = K or Cs) [37]. Addition of a copper(I) compound or complex will provide the tin-copper or cuprate species.

Various organic chlorides, bromides, iodides and tosylates, R¹X, react with R₃SnM. Particularly clean reactions occur with primary and secondary alkyl halides but eliminations can become troublesome with tertiary alkyl halides. However, it is possible to obtain tertiary alkyltin compounds, as shown by the formation of 1-trimethylstannyladamantane [38].

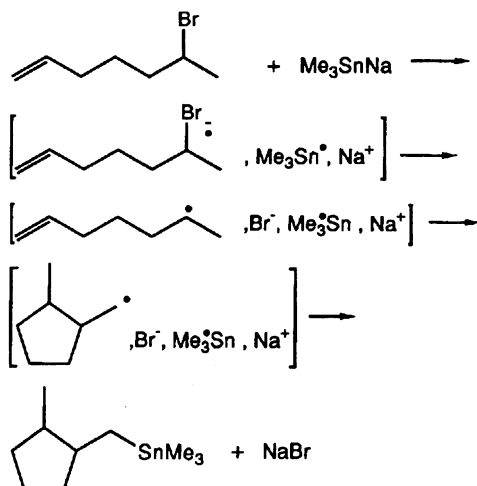


The mechanisms of secondary alkyl halide reactions, such as reactions 4.14 and 4.15, have attracted considerable attention [39; see also 40–46].

As shown in eqn 4.15 and in cyclopropylcarbinyl halide/R₃SnM reactions, rearrangements, indicative of radical intermediates, can occur [30] (Scheme 4.1).



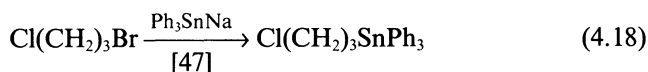
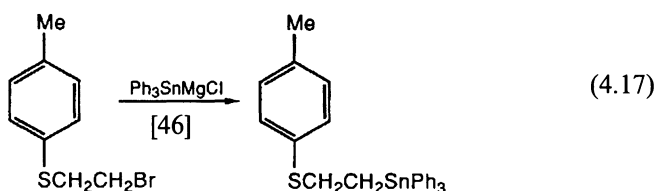
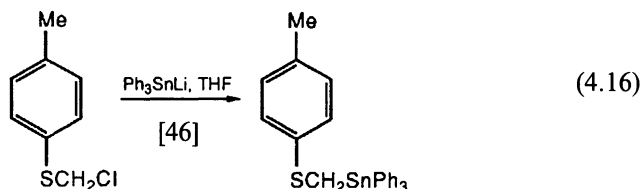
Three pathways have been indicated, namely (1) an S_N2 type substitution with inversion of configuration; (2) an electron transfer (or radical pair) mechanism for the more readily reduced organic halides, which can lead to rearrangements; and (3) substitution, with overall retention of configuration, occurring via an initial halogen-metal exchange (e.g. as found in reactions of secondary cyclopropyl bromides) [45]. Even electron transfer processes can proceed with predominant inversion of configuration [39; see also 40–44].



Scheme 4.1

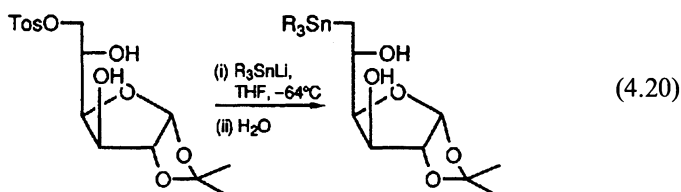
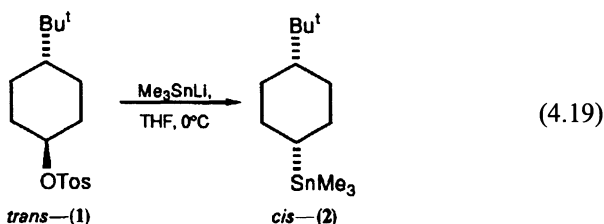
Temperature, solvent, halide and method of preparation of R_3SnM (and consequently the presence of additional species, such as RM or M) affect the situation.

Functionally substituted alkyl halides can be used to generate the corresponding tin compounds, e.g. eqns 4.16–4.18.

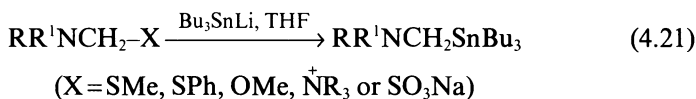


Reaction 4.18 indicates the greater reactivity of Br over Cl. Other α - and β -substituted alkyltins (e.g. substituent = α -MeO, β -(EtO) $_2$ PO, β -R $_2$ N and β -RCO) have been obtained from the corresponding alkyl halides [35].

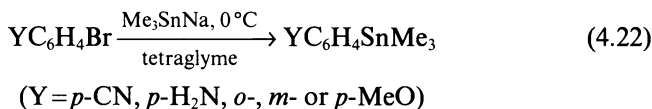
Alkyl tosylates react readily with R_3SnM and proceed with complete inversion of configuration, e.g. eqns 4.14 and 4.19; *cis*-(1) reacts similarly to give *trans*-(2). Use of the tosylate substitution has been made in the carbohydrate field (J.L. Wardell and C. Welsh, unpublished results), eqn 4.20.



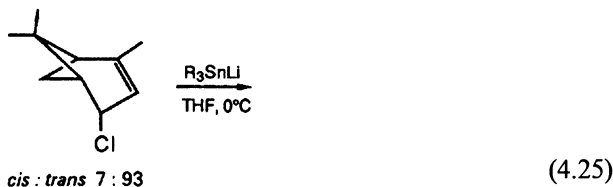
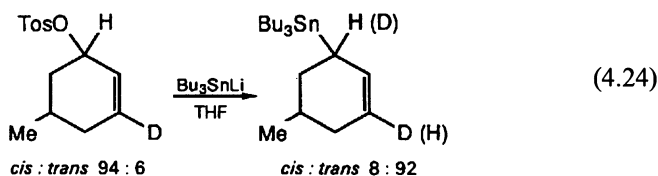
Leaving groups other than halides and tosylates have found limited use [48, 49], e.g. eqn 4.21.



Aryl bromides react, in the main, regiospecifically with R_3SnLi (eqn 4.22), whereas *cine*-substitution can occur to a limited extent with aryl chlorides or fluorides [35, 50]. Aryne and free radical intermediates [51] as well as metallations of the aryl halide by the RLi , present with the R_3SnLi , have been indicated in the *cine*-substitutions. Various substituents, sensitive to RM , survive these aryl halide- R_3SnM reactions. Some evidence has been found for an initial metal-halogen exchange preceding the formation of the aryl-tin bond [35] (eqn 4.23). For hindered aryl bromides, such as 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{Br}$, products of free radical processes have been detected [52].

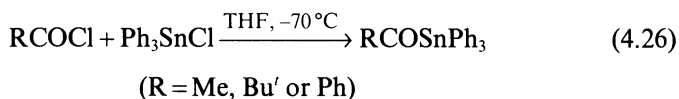


Triorganostannyl alkali compounds have been also shown to react with heteroaryl halides, vinyl halides (usually with predominant retention of configuration), propargyl bromides (which provide allenyltins) and allyl halides or tosylates, e.g. eqns 4.24 and 4.25. For primary allyl halides, allylic rearrangements do not arise, but these can result with secondary compounds.

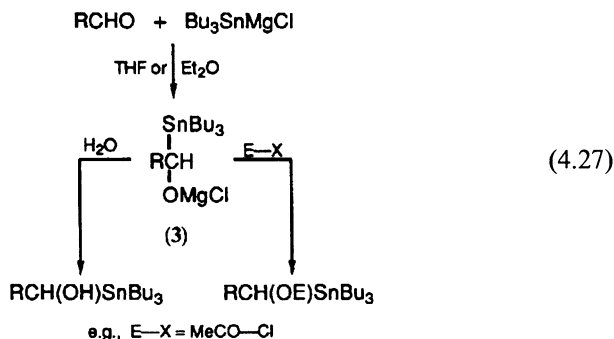


R = Me; *cis* : *trans* 32 : 64
R = Ph; *cis* : *trans* 59 : 29

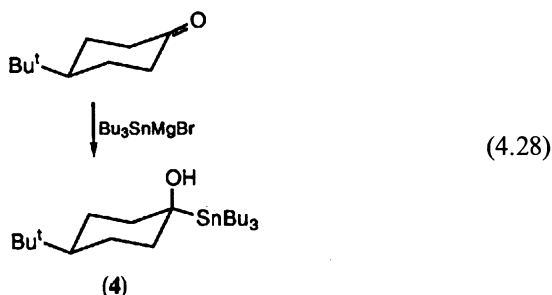
Acyl chlorides react to give acyltins at low temperature [53; see also 54] (eqn 4.26):



Aldehydes and ketones react [35, 55] with R_3SnM (M = Li or MgCl), to give good yields of α -hydroxyalkyltins, especially in Et_2O or THF. The intermediate alkoxide (3) can be trapped by electrophiles other than the proton (eqn 4.27).

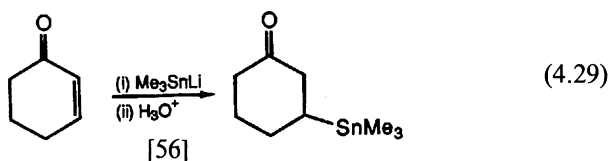


Use of excess RCHO leads to formation of RCOSnBu_3 and RCH_2OH . The bulky Bu_3Sn group goes into the equatorial site on reaction with the cyclohexanone [35] (4). As simple addition occurs to cyclopropylmethylketone, an electron transfer mechanism can be ruled out [35].

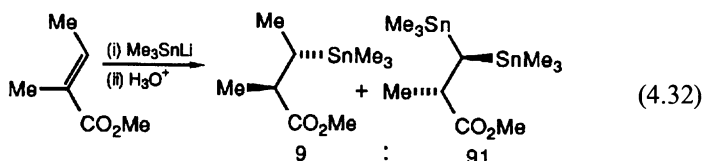
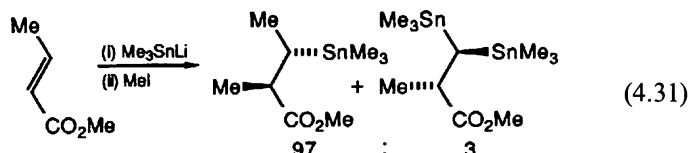
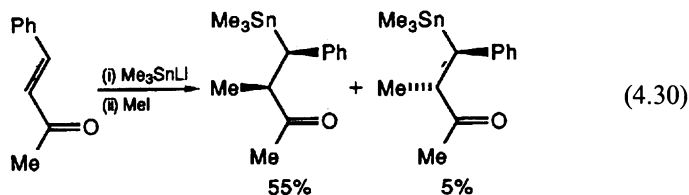


Both 1,2- and 1,4-additions occur with β -enones; to RCH=CHCOR' ; 1,4-additions occur with Bu_3SnMgCl in Et_2O , R_3SnLi (e.g. eqn 4.29 [56]) or $(\text{R}_3\text{Sn})_2\text{CuLi}$, whereas 1,2-adducts have been isolated from $\text{RR}^1\text{C=CHCOR}^2$. There is some evidence to suggest that the kinetic products are the 1,2-adducts which can rearrange to the thermodynamically more stable 1,4-adducts, especially on raising the reaction temperature and in more polar solvents [35]. For addition of R_3SnNa , the use of a protic solvent is recom-

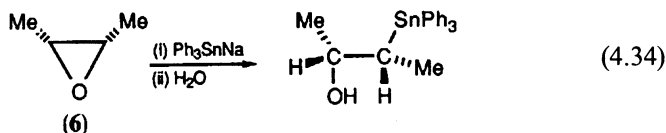
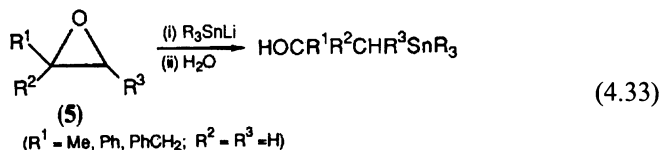
mended to trap the intermediate enolate as it is formed and before it undergoes condensation reactions [57].



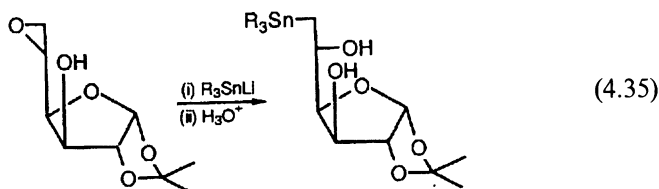
Reasonably good stereoselectivities are observed [58; see also 59] in the 1,4-addition reaction as shown in eqns 4.30–4.32.



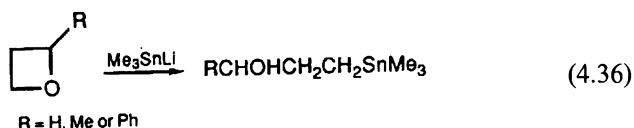
Reactions with epoxides provide β -hydroxyalkyltins (eqn 4.33) [23, 35, 36, 58–65]. The regioselectivity is less for trisubstituted epoxides (**5**, $\text{R}^3=\text{R}^2=\text{R}^1=\text{alkyl}$) [62]. The *trans* isomer was obtained from cyclohexene oxide [60, 63; see also 64]; ring opening of the 1,2-*cis*-dimethyl epoxide (**6**) occurs with inversion of configuration [65] (eqn 4.34).



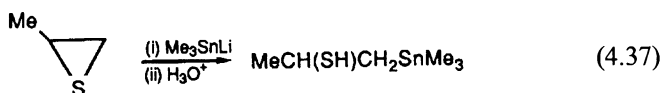
Use of the epoxide opening has also been made with carbohydrates [58; see also 59] (eqn 4.35).



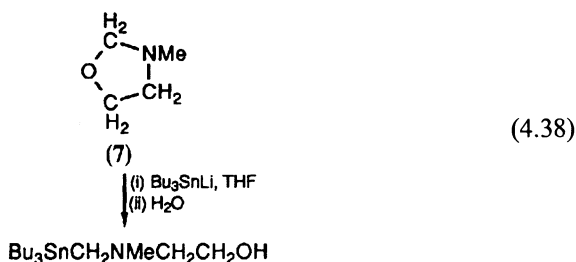
Reactions of oxetanes with R_3SnM lead to γ -hydroxyalkyltins [62] (eqn 4.36).



For the sulphur ring analogues, desulphurization and attack at sulphur can limit the yields of β - and γ -mercaptoalkyltin products. 1-Methylthiirane, however, provides a good yield of the 2-mercaptopropyltin species [62] (eqn 4.37).

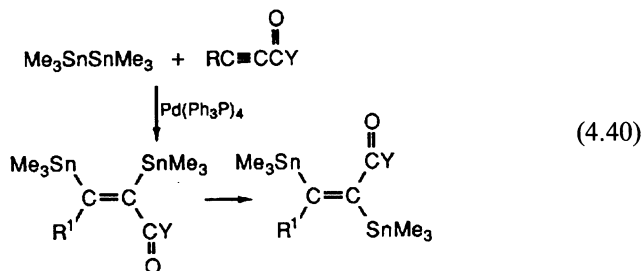
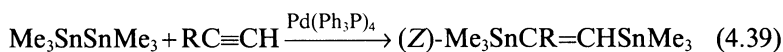


Ring opening [48, 49] also occurs with the heterocycle (7), eqn 4.38.

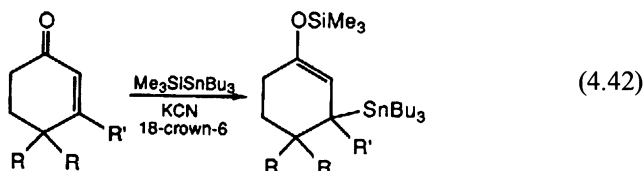
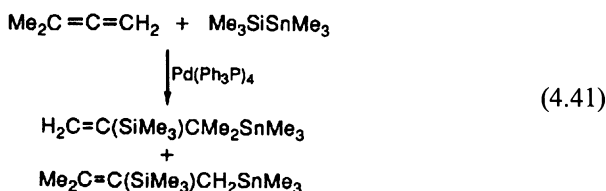


Triorganostannyl anionic compounds [R_3SnM , $\text{M} = \text{MgMe}$, AlEt_2 or $\text{Zn(SnR}_3\text{)}$] add to alkynes in the presence of copper or palladium catalysts [66]. These and related additions of triorganostannyl-copper and cuprates are discussed in section 4.1.2. (Vinylstannanes).

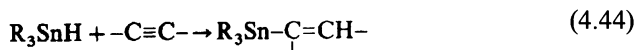
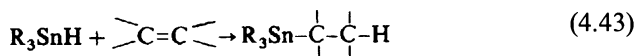
From other metal-tin compounds. Both distannanes, R_3SnSnR_3 [67, 68], and stannylsilanes R_3SnSiR_3 [69, 70], add in a *cis* manner to alkynes, in the presence of $\text{Pd(Ph}_3\text{P)}_4$, e.g. eqns 4.39 and 4.40.



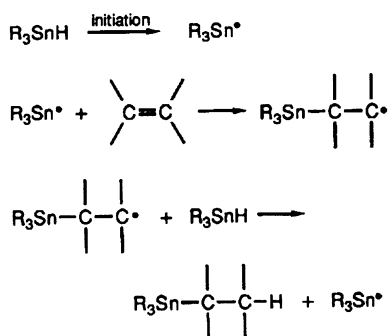
Stannylsilanes also add to allenes [69, 71] (e.g. eqn 4.41 [69]) and β -enones [70, 72] (eqn 4.42).



Hydrostannation of alkenes and alkynes [1, 73–76]. Organotin hydrides add to alkenes and to alkynes (eqns 4.43 and 4.44):



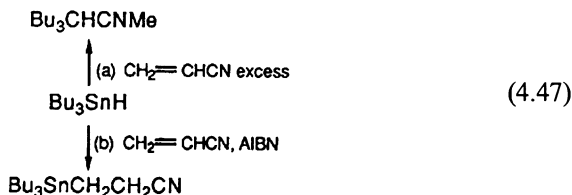
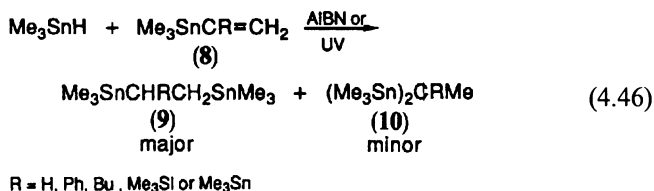
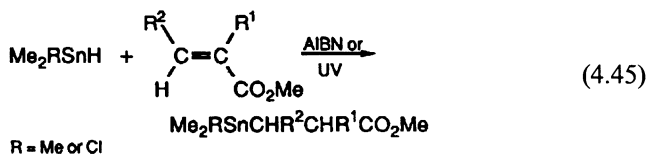
Unless strongly electron-withdrawing groups are present in the unsaturated species, the additions are free radical chain processes. The key steps for alkene additions are shown in Scheme 4.2. Additions to terminal alkenes and alkynes occur readily, usually on UV irradiation or in the presence of a radical initiator, such as AIBN. For non-terminal species, the reactions are best carried out on UV irradiation unless these are activated by strain [77] or have substituents able to stabilize the intermediate organyl radical.



Scheme 4.2

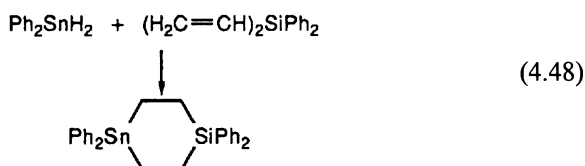
Usually for 1-alkenes, tin adds predominantly to the terminal carbon, e.g. eqns 4.45 [78] and 4.46, although for (**8**; R=H or Me₃Sn), appreciable amounts of the non-terminal adduct (**10**), are formed (in *c.* 40% yield compared to <5% for the other R groups) [79, 80]. The regioselectivity of addition to acrylonitrile is dependent on the conditions and whether a nucleophilic (a) [79] or radical (b) [80] mechanism applies (eqn 4.47) [74].

Various, other functional groups can be tolerated, and hydrostannation is a particularly valuable route to substituted alkyltins, bearing functional groups in β-, γ- or more remote positions, using CH₂=CH(CH₂)_nX (X=SR, SO₂R, OR, PR₂, P(OR)₂, etc.) (see Tables 4.2–4.5 for examples). Amines [74]



and sulphoxides [81] catalyse decomposition of tin hydrides to distannanes, and so tin compounds containing such groups cannot be prepared by this route.

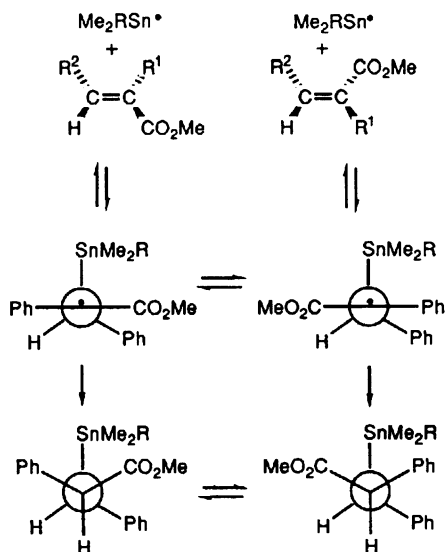
As well as R_3SnH , other tin hydrides which can be used include R_2SnH_2 [82], R_3SnH_3 and R_2SnHCl (eqn 4.45). The use of UV irradiation is recommended for R_2SnHCl reactions. Additions to R_2SnH_2 occur stepwise, and the mono-adducts can be trapped. For non-conjugated dienes, addition of R_2SnH_2 can lead to heterocycles [83; see also 84], e.g. eqn 4.48.



Hydrostannation of bifluoroenylidene with chiral methylphenylneophyltin hydride takes place with some retention of configuration, implying that the intermediate tin radical is captured before it can become planar [85]. Some asymmetric induction (10–20% ee) has been obtained [86] in the reaction of (–)-methyl crotonate and Bu_3SnH .

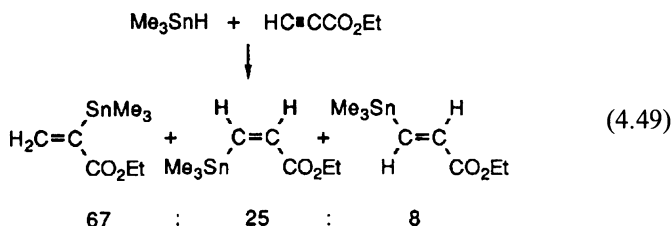
In eqn 4.45, two chiral centres are generated [78]; diastereomeric mixtures are obtained, in which the *erythro* isomer predominates. Both (*Z*)- and (*E*)- $R^2CH=CR^1CO_2Me$ isomers provide the same product composition, resulting from the reversibility of the free-radical formation step (Scheme 4.3) [87–89].

Hydrostannation of terminal alkynes [74] containing a strongly electron-



Scheme 4.3

withdrawing group, e.g. CO_2R or CN , produces mainly, and possibly exclusively, the α -adduct via an ionic mechanism, e.g. eqn 4.49. Addition to compounds bearing an electron-releasing group, such as an alkyl or alkoxy group, or a weakly electron-withdrawing group, e.g. CH_2OH or Ph , yields mainly the *cis* and *trans* β -adduct (via a free radical mechanism) as well as small amounts of the α -adduct. Initial additions occur in a *trans* manner (to give the *cis* adducts) with subsequent isomerizations of the *cis*- $\text{R}_3\text{SnCH}=\text{CHR}^1$ resulting to give the thermodynamically more stable *trans* isomers, via radical intermediates. Hydrostannation of non-terminal alkynes by trialkyltin hydrides affords mainly the *trans* adducts. Heterocycles can also be produced, e.g. from $\text{HC}\equiv\text{CCH}_2\text{C}\equiv\text{CH}$ and Bu_3SnH_2 .

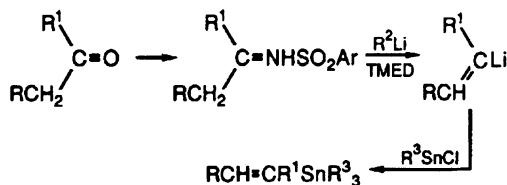


Metallation of acidic hydrocarbons by tin-oxygen and tin-nitrogen bonded compounds [1, 23]. Acidic hydrocarbons can be metallated by R_3SnNMe_2 , $(\text{R}_3\text{Sn})_2\text{O}$ and related compounds; tin amides appear to be the more reactive. Hydrocarbons which can be metallated include alkynes, polyhaloalkanes, polyfluoroarenes, $\text{HN}_2\text{CCO}_2\text{Et}$, cyclopentadiene and fluorene as well as HCR_2Y ($\text{R}=\text{H}$ or alkyl; $\text{Y}=\text{CN}$, NO_2 , CONR_2 , COR or SO_2Ph), e.g. eqn 4.50 [90].

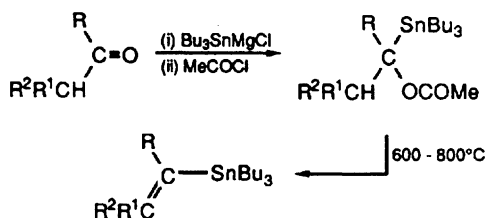


4.1.2 Formation of specific types of organotin compounds

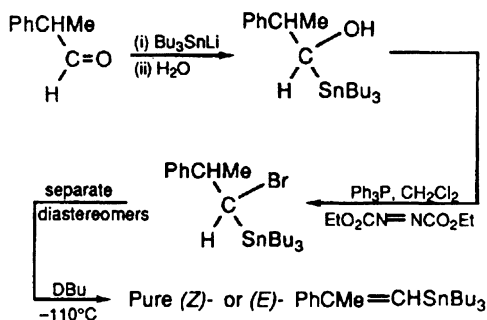
Vinylstannanes. Vinylstannanes are generated from the corresponding vinyl-Grignards and vinyl lithium compounds with retention of configuration [91]. Vinyl halides, substituted alkenes and arenesulphonyl hydrazones [92] (Scheme 4.4 and eqn 4.9) are useful sources of the vinyl-metal [27]. Scheme 4.4 illustrates a method of synthesis from ketones; other routes from ketones are shown in Schemes 4.5 [93; see also 94, 95] and 4.6 [96].



Scheme 4.4

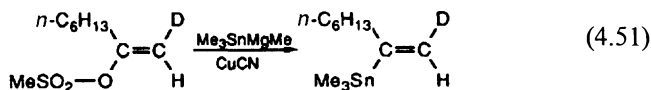


Scheme 4.5



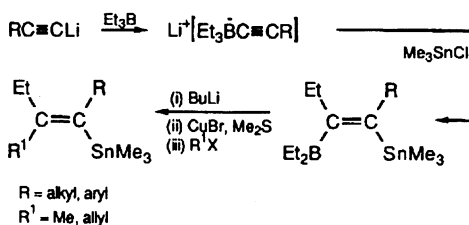
Scheme 4.6

Reactions of vinyl halides and triflates with triorganostannyl anions produce vinylstannanes [35, 97–99]. Reactions of $\text{Me}_3\text{SnMgMe/CuCN}$ with vinyl triflates, but not iodides, are stereospecific (eqn 4.51) [66].



Hydrostannylation of alkynes provides vinylstannanes (section 4.1.1); however, these reactions are not always stereospecific [100–102]. In addition, certain isomers dominate and, as these may not be the ones required, use has been made of other methods involving alkynes.

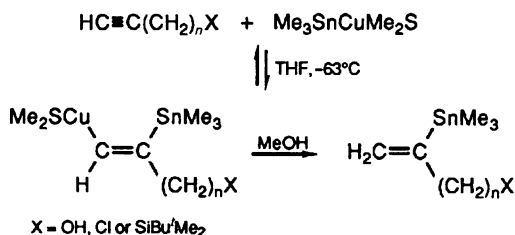
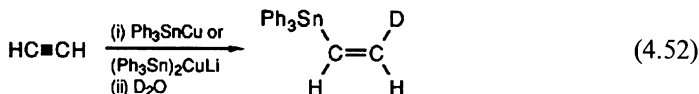
Alkynylborates can be used in very stereoselective (>98%) syntheses (Scheme 4.7) [103, 104].



Scheme 4.7

Triorganotin-metal compounds, including R_3SnSnR_3 , R_3SnSiR_3 , $Bu_3SnAlEt_2$, $(Bu_3Sn)_2Zn$ and triorganotin copper reagents, add in a *cis* manner to alkynes.

Triorganotin copper(I) species add to terminal alkynes (eqn 4.52 and Scheme 4.8) [105, 106].

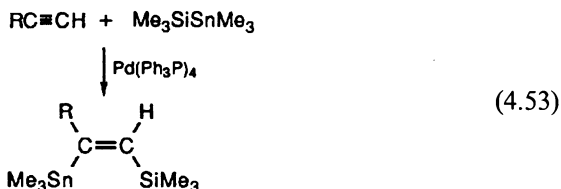


Scheme 4.8

Additions also occur to $HOCH_2C\equiv CCH_2OH$ using $Bu_3SnCu \cdot SMe_2 \cdot LiBr$ providing (*E*)- $HOCH_2CH=C(SnBu_3)CH_2OH$ [107]. An interesting ditin product, (*E*)- $RC(SnMe_3)=C(SnMe_3)CO_2R'$, was isolated from $RC\equiv CCO_2R'$ and excess $(Me_3Sn)_2CuLi$ at $-48^\circ C$ in THF [108].

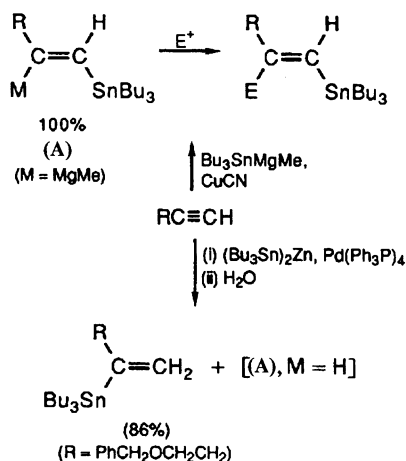
As shown in eqns 4.39 and 4.40, ditins add to alkynes [67, 68]. The initial (*Z*)- $Me_3SnCR=CXSnMe_3$ products ($X=H, CO_2R$ or $CONMe_2$) readily isomerize to the (*E*)-alkenes on UV irradiation (for $X=H$) or thermally (for $X=CO_2R'$ or $CONMe_2$).

The addition of stannylsilanes to terminal alkynes [69, 71] are regio- and stereospecific, e.g. eqn 4.53.

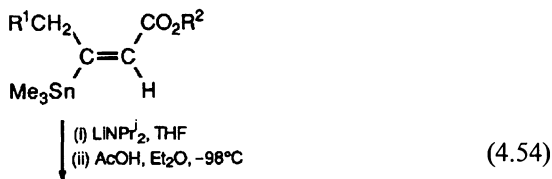


Different regioselectivities are obtained in the palladium-catalysed stannylzincation and in the copper-catalysed stannylmagnesiumation [66] of $HC\equiv C(CH_2)_2OCH_2Ph$ (Scheme 4.9).

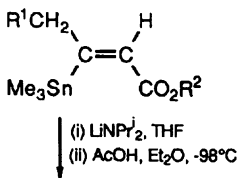
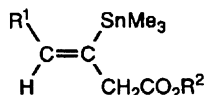
The stereospecific isomerization of $R'CH_2C(SnMe_3)=CHCO_2R^2$ (R' =alkyl or $R_3SiOCH_2CH_2$) to $R'CH=C(SnMe_3)CO_2R^2$ has been devised (eqns 4.54 and 4.55) [109].



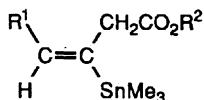
Scheme 4.9



(4.54)

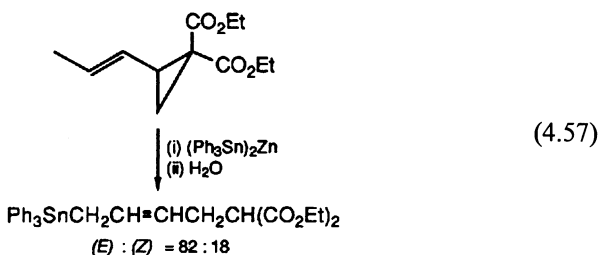
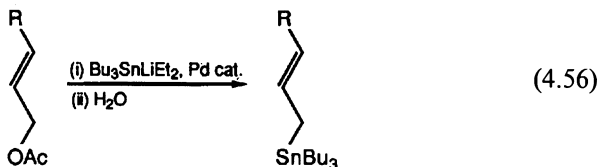


(4.55)

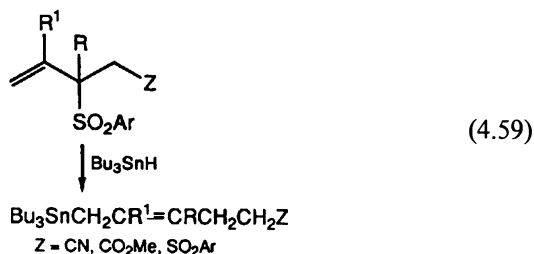
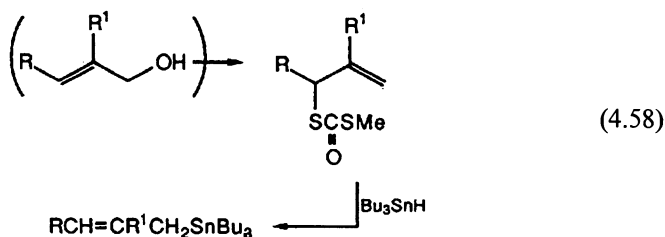


Allylstannanes. Allylstannanes have been obtained both from reactions of allylmagnesium or allyllithium compounds with organotin halides or even oxides [110–112] and from triorganotin anionoid compounds (R_3SnM) with alkenyl halides or esters [35, 113, for related systems see 114] (G. Dumardin, J.-P. Quintard and M. Pereyre, unpublished observations, quoted in Ref. 35)

(eqns 4.24, 4.25 and 4.56). Reaction 4.56 occurs with high regio- and stereo-selectivity [115]. A 1,7-homoconjugate addition of $(\text{Ph}_3\text{Sn})_2\text{Zn}$ produces an allylstannane (eq 4.57) [116].

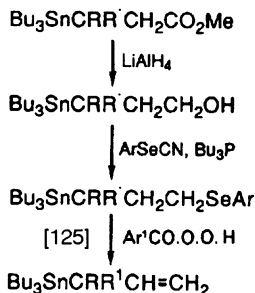
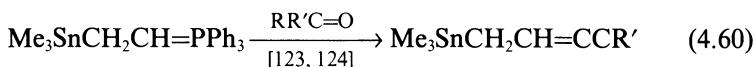


Various allylic derivatives (e.g. sulphones, xanthates, sulphides and tosylates [117–121]) react with organotin hydrides to give allylstannanes, e.g. eqns 4.58 and 4.59.



These reactions are, however, not usually stereospecific. Hydrostannation of 1,3-dienes also produces allylstannanes [122].

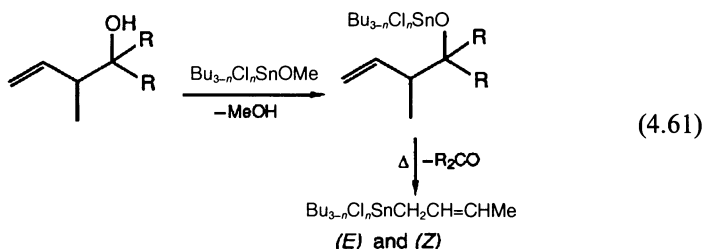
Modifications of existing functionally substituted organotins have been used, e.g. eqn 4.60 and Scheme 4.10.



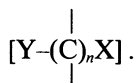
Scheme 4.10

As shown in Scheme 4.10, α -substituted allyl compounds are obtained, in contrast to other synthetic methods which generate γ - or α/γ mixtures.

Addition of allylstannanes to ketones is a reversible reaction, and hence pyrolysis of homoalkyl enolates can be utilized in the synthesis of allylstannanes (eqn 4.61) [126].

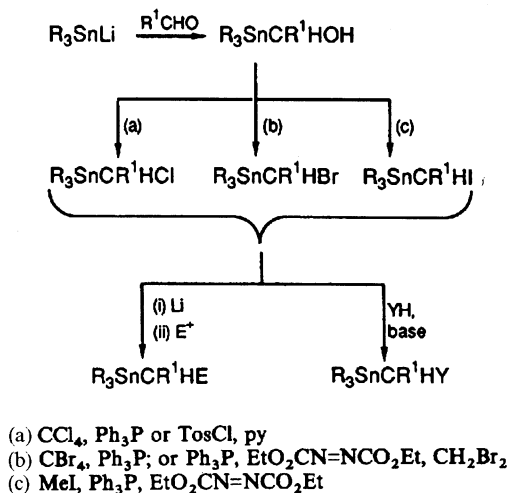


Functionally substituted allylstannanes. Functionally substituted alkylstannyl species constitute a useful but wide and disparate range of compounds. All the general routes discussed earlier can be used to advantage, e.g. (1) the use of organotin halides plus $\text{YCR}^1\text{R}^2\text{Li}$ reactions (e.g. Y =nitrogen, phosphorus, sulphur, selenium, halo, cyano or carbonyl group) for α -substituted derivatives; (2) hydrostannation of vinyl compounds, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{Y}$ for β , γ or δ derivatives (Y =oxygen, sulphur, phosphorus, carbonyl groups, etc.); and (3) reactions of R_3SnM and substituted alkyl halide



Clearly specific routes also have to be devised, and modifications of existing functional groups have been used to great effect, as follows:

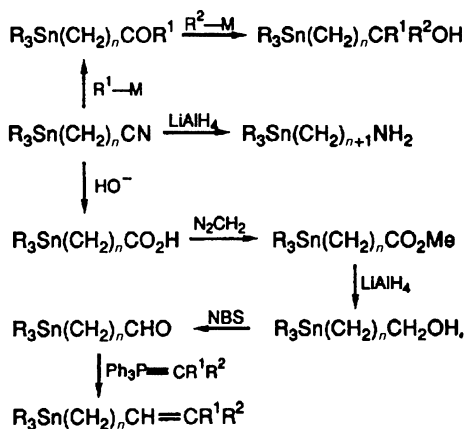
- By conversion of hydroxyl groups to halogen groups with the possibility of further substitutions (e.g. Scheme 4.11); [related reactions occur for $R_3Sn(CH_2)_nOH$, $n > 3$].



Scheme 4.11

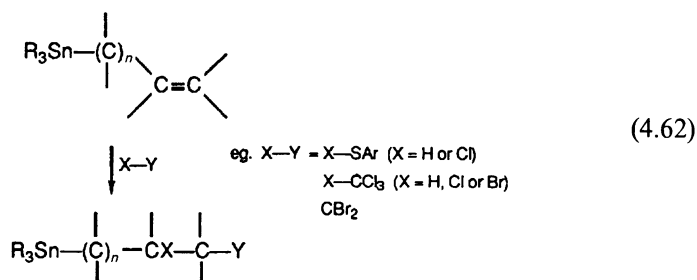
$E' = CH_2CH_2OH$ or CR^1R^2OH ; $Y = OR^2$, SR^2 , SO_2R^2 , SeR^2 , NR_2^2 , etc.

- By conversion of cyano and carbonyl derivatives, e.g. Scheme 4.12:



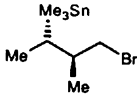
Scheme 4.12

- By oxidations, e.g. of sulphur and phosphorus groups, as well as carbon groups, e.g. Scheme 4.12.
- On addition to vinyl- and 3-butenylstannanes by electrophiles, free radicals and carbenes (eqn 4.62).



Examples of these and other methods of preparation are given in Tables 4.1–4.7.

Table 4.1 Preparation of haloalkyltin compounds

Compound	Reagents	Ref.
$\text{R}_3\text{SnCHR}'\text{I}$ ($\text{R}' = \text{H}$ or Me_3Sn)	R_3SnI , $\text{ICHr}'\text{ZnI}$	1
$\text{R}_2\text{Sn}(\text{CH}_2)_2$	R_2SnI_2 , ICH_2ZnI	1
$\text{R}_3\text{SnCH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br or I)	R_3SnX , N_3CH_2	2
$\text{R}_3\text{Sn}(\text{CH}_2)_n\text{Cl}$ ($n = 1, >3$)	$\text{R}_3\text{Sn}(\text{CH}_2)_n\text{OH}$, CCl_4 , PPh_3	3
$\text{Bu}_3\text{SnCHRCI}$	(i) Bu_3SnLi , RCHO	4
	(ii) TosCl , py	7
$\text{Bu}_3\text{SnCHRBBr}$	(a) $\text{Bu}_3\text{SnCHROH}$, CBr_4 , Ph_3P	4
	(b) $\text{Bu}_3\text{SnCHROH}$, Ph_3P , $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$, CH_2Br_2	5
Bu_3SnCHRI	$\text{Bu}_3\text{SnCHROH}$, Ph_3P , $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$, MeI	4
	(i) LiAlH_4	6
	(ii) TosCl	
	(iii) LiBr	
$\text{Bu}_3\text{Sn}(\text{CH}_2)_n\text{Br}$ ($n > 3$)	SnCl_2 , $\text{Br}(\text{CH}_2)_n\text{Br}$, R_3Sb	7
$\text{R}_3\text{SnCX}_2\text{X}'$ ($\text{X} = \text{X}' = \text{halide}$)	(a) R_3SnCl , $\text{LiCX}_2\text{X}'$	8
	(b) R_3SnBr , $\text{PhHgCX}_2\text{X}'$	
$\text{Et}_3\text{SnCHXCH}_2\text{CCl}_3$ ($\text{X} = \text{H}$, Cl or Br)	$\text{Et}_3\text{SnCH}=\text{CH}_2$, XCCl_3 , $(\text{PhCO}_2)_2$	9

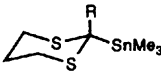
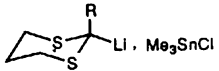
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Table 4.2 Hydroxy- and alkoxy-alkyltin compounds

Compound	Reagents	Ref.
$R_3SnCHR'OH$	$R_3SnLi, R'CHO$	1
	, Bu_3SnLi	2
Ph_3SnCH_2OR	$Ph_3SnCH_2I, NaOAr$	3
	, $Bu_3SnMgCl$	4
$R_3SnCH_2CH_2OR'$	$R_3SnH, CH_2=CHOR'$	5, 6
	, Me_3SnLi	7: see also 8
$R_3Sn(CH_2)_nOH$	$R = Me, n = 3-6$ (a) $Me_3SnH, CH_2=CH(CH_2)_{n-2}OH$ (b) $R = Ph, n = 3-5; Ph_3Sn(CH_2)_{n-1},$ $CO_2Me, LiAlH_4$	9
$R_3SnCH_2CH_2CH_2OR'$	$R_3SnH, CH_2=CHCH_2OR'$	5, 6
	, $LiAlH_4$	7: see also 8
<i>cis : trans</i> $Bu_3SnCH_2CHPhCMe_2OH$	$Bu_3SnCR_2CH_2C(O)R^2,$ R^1Li or R^1MgX	10-14
$Bu_3SnCH_2CHPhCMe_2OH$	$Bu_3SnCH_2CHPhCO_2Me, MeLi$	10
$Me_3Sn(CH_2)_3CHPhOH$	$Me_3Sn(CH_2)_3Br$ (i) Mg (ii) $PhCHO$ (iii) H_2O	15
	(i) Me_3SnLi (ii) H_2O	7: see also 8

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Table 4.3 Sulphur-containing alkylltin compounds

Compound	Reagents	Ref.
R_3SnCH_2SR'	(a) R_3SnLi , $ClCH_2SR'$ (b) R_3SnCH_2I , HSR'	1, see also 2, 3 1, see also 2, 3; 4
$Bu_3SnCH(SiMe_3)SPh$	$LiCH(SiMe_3)SPh$, Bu_3SnCl	5
	 Li , Me_3SnCl	6, 7
Bu_3SnCH_2SOR ($R = Me, Ph$)	Bu_3SnNMe_2 , $MeSOR$	8
$Bu_3SnCH_2SO_2R$ ($R = alkyl, Ph, NMe_2$)	(a) MCH_2SO_2R , ($M = Li, BrMg$) Bu_3SnCl (b) Bu_3SnNEt_2 , $MeSO_2R$	9, 10
$Bu_3SnCH_2S^+Me_2X^-$	Bu_3SnCH_2SMe , MeX	5
$Bu_3SnCH_2CH_2SH$	$Bu_3SnCH=CH_2$, H_2S	11
$Me_3SnCH_2CHMeSH$	Me_3SnLi , $MeCHCH_2S$	12
$R_3SnCH_2CH_2SR'$	(a) $R_3SnCH=CH_2$, HSR' (b) R_3SnH , $CH_2=CHSR'$	1, see also 2, 3; 13, 14
$R^1R^2C=CR^3CH(SAr)CH_2SnBu_3$ ($Ar = 2$ -pyridyl)	$R^1R^2C=CR^3CH(SAr)Li$, Bu_3SnCH_2I	15
$Ph_3SnCH_2CH_2SO_2R$	Ph_3SnH , $CH_2=CHSO_2R$	16, 17
$Bu_3SnCHR^2CHR^1SO_2Ph$	Bu_3SnLi , $R^2CH=CR^1SO_2Ph$	18
$R_3Sn(CH_2)_3SR'$	$R_3Sn(CH_2)_3Cl$, HSR'	19, see also 20
$Ph_3Sn(CH_2)_nSO_mR'$ ($n = 3, 4$; $m = 1, 2$)	$Ph_3Sn(CH_2)_nSR'$, m - $C_6H_4CO\cdot OOH$	16, 17
$Ph_3Sn(CH_2)_4SR'$	(a) $Ph_3Sn(CH_2)_2CH=CH_2$, HSR' (b) Ph_3SnH , $H_2C=CH(CH_2)_2SR'$	19, see also 20
$Bu_3SnCH_2CH(CH_2R')S(O)Ph$	Bu_3SnCH_2I , $R^1CH_2CHLiS(O)Ph$	21
Ph_3SnCH_2SeR'	Ph_3SnCH_2I , $HSeAr$	22

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Table 4.4 Amino group substituted alkyltin compounds

Compound	Reagents	Ref.
$R_3SnCH_2NR'_2$	(a) R_3SnCH_2I , R'_2NH	1
	(b) R_3SnLi , R_2NCH_2X ($X = SR_2$, SO_2Na)	2
	(c) R_3SnCH_2Cl , MNR'_2 ($M = H$ or K)	3
$(Bu_3SnCH_2)_2N$	$(PhSCH_2)_3N$, Bu_3SnLi	1
$R_3SnCH_2CH_2NR'_2$ ($R' = H$, alkyl or aryl)	R_3SnM ($M = Na$ or Li), $ClCH_2CH_2NR'_2$	4–6
$R_3SnCH_2CH_2CH_2NH_2$	$R_3SnCH_2CH_2CN$, $LiAlH_4$	7
$R_3SnCH_2CH_2CH_2NMe_2$	(a) $R_3SnCH_2CH_2CH_2NH_2$, HCO_2H , H_2CO	7
	(b) R_3SnLi , $ClCH_2CH_2CH_2NMe_2$	8
$MeSn(CH_2CH_2CH_2)_3N$	$MeSnCl_3$, $(ClMgCH_2CH_2CH_2)_3N$	9
$Bu_3Sn(CH_2)_nNMe_2$ ($n = 3, 4$)	$Bu_3Sn(CH_2)_nBr$, Me_2NH	10
$R_3Sn(CH_2)_nN^+R'_2R''^2$, I^-	$R_3Sn(CH_2)_nNR'_2$, R''^2I	11 ^a
$Ph_3SnCH_2CH_2CH_2NHCOMe$	Ph_3SnH , $CH_2=CHCH_2NHCOMe$	12
$Ph_2ClSnCH_2CH_2CH_2NHCOMe$	$Ph_2ClSnCH_2CH_2CH_2CMe=NOH$	13

^aAlso J.L. Wardell, unpublished observations.

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Table 4.5 Phosphorus-containing alkyltin compounds

Compound	Reagents	Ref.
$Me_nSn(CH_2PMe_2)_4-n$	Me_nSnCl_4-n , $LiCH_2PMe_2$	1
$Ph_3SnCH_2P(S)Ph_2$	$Ph_2P(S)CH_2Li$, Ph_3SnCl	2
$R_3SnCH_2P(O)(OR')R^2$ ($R' = Me$, Et ; $R^2 = OR'$, Ph)	(a) R_3SnCH_2I , $P(OR')_2R^2$	3
	(b) R_3SnH , $N_2CHP(O)(OR')R^2$	
	(c) R_3SnNa , $ClCH_2P(O)(OR')R^2$	
	(d) R_3SnNMe_2 , $CH_3P(O)(OR')R^2$	
$Me_3SnCHRP(Y)(OR')_2$ ($Y = O$, S)	Me_3SnCl , $(R'O)_2P(Y)CHRCu$	4
$Ph_3SnCHRPPh_3$, Cl^- ($R = H$, Me , Pr)	Ph_3SnCl , Ph_3PCHR	5
$Me_3SnCX = PC_6H_2Bu'_3$ ($X = Cl$, Br)	Me_3SnCl , $LiCX = P-C_6H_2Bu'_3$	6
$R_3SnCH_2CH_2PR'_2$	R_3SnH , $R'_2PCH=CH_2$	7
$Ph_3SnCH_2CHPhPPh_2$	Ph_3SnPPh_2 , $CH_2=CHPh$	8
$Et_3Sn(CH_2CH_2PPhR')_2$ ($R' = Ph$, Bu)	Et_3SnH_2 , $CH_2=CHPPhR'$	9
$Me_3Sn(CH_2)_{n+2}PR'R^2$ ($n = 0, 1$)	(a) Me_3SnH , $CH_2=CH(CH_2)_nPR'R^2$	10
	(b) Me_3SnNa , $Cl(CH_2)_{n+2}PR'R^2$	
$R_2R'SnCH_2CH_2P(O)R^2Ph$ ($R^1 = Me$, Ph ; $R = Me$, Bu) ($R^2 = Bu$, OEt)	(a) $R_2R'SnH$, $CH_2=CHP(O)(OEt)Ph$	11
	(b) (i) $CH_2=CHPPhBu'$, $R_2R'SnH$	
	(ii) $KMnO_4$	
$Et_2Sn[CH_2CH_2P(S)PhR']_2$	$Et_2Sn[CH_2CH_2PPhR']_2$, S	9
$[Et_2Sn(CH_2CH_2PPhR'Me)]_2^{2+}2I^-$	$Et_2Sn(CH_2CH_2PPhR')_2$, MeI	9
$Et_3Sn(CH_2)_{n+2}P(O)(OEt)R$ ($n = 0, 1$; $R = EtO$, Ph)	Et_3SnH , $CH_2=CH(CH_2)_nPO(OEt)R$	12
$R_3SnCHMeCH=PPh_3$	R_3SnLi , $MeCH=CH^+PPh_3$, Br^-	13

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Table 4.6 Cyanoalkyltin compounds

Compound	Reagents	Ref.
R_3SnCH_2CN	(a) R_3SnCl , $NaCH_2CN$	1
	(b) $Ph_3SnOCOCH_2CN$, Δ	2
$Ph_3SnCHCNMe$	$Ph_3SnOC(O)CHCNMe$, Δ	3
$R_3SnCH_2CH_2CN$	R_3SnH , $CH_2=CHCN$	3
$Ph_3SnCH_2CH_2CH_2CN$	Ph_3SnH , $CH_2=CHCH_2CN$	3, 4
$Me_3Sn(CH_2)_{n+2}CN$	Me_3SnH , $CH_2=CH(CH_2)_nCN$	5

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Table 4.7 Carbonyl- and carboxyl-substituted alkyltins

Compound	Reagents	Ref.
Bu_3SnCOR	(a) $Bu_3SnMgCl$, excess $RCHO$ (b) Bu_3SnLi , $EtCOBr$ (c) $Bu_3SnSnBu_3$, $EtCOCl$, Pd^0	1
R_3SnCH_2COR'	(a) R_3SnH , N_2CHCOR' (b) $(R_3Sn)_2$, $Hg(CH_2COR')_2$	2
$Cl_3SnCHMeCOEt$	$SnCl_4$, $Et(Me_3SiO)C=CHMe$	3
$Bu_3SnCH_2CH_2CHO$	$Bu_3SnCH_2CH_2CH_2OH$, NBS, Me_2S	4
$Pr_3SnCH_2CH_2COMe$	$CH_2=CHCN$ (i) Pr_3SnH (ii) $MeMgI$	5
$Cl_3SnCH_2CH_2COBu'$	$Bu'[(Me_3SiO)CCH_2CH_2]_2$, $SnCl_4$	6
$Cl_3SnCMe_2CH_2COMe$	$SnCl_2$, HCl , Me_2CO (excess)	7
	$SnCl_2$, HCl , mesityl oxide	8
$Me_3Sn(CH_2)_{n+2}COR$	(a) $n = 0, 1, 2$; (i) Me_3SnH , $CH_2=CH(CH_2)_nCHOHMe$ $R = Me$ (ii) CrO_3 , Me_2CO (b) $n = 0, 1$; (i) Me_3SnH , $CH_2=CH(CH_2)_nCN$ 10, 11 $R = Me$ or Ph (ii) $RMgX$	9, 10, 11

Table 4.7 *Cont'd*

Compound	Reagents	Ref.
		12
$\text{Ph}_3\text{Sn}(\text{CH}_2)_4\text{COMe}$	Ph_3SnH , $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{COMe}$	13
		14
$\text{R}_3\text{Sn}(\text{CH}_2)_3\text{CMe}=\text{NOH}$	$\text{R}_3\text{Sn}(\text{CH}_2)_3\text{COMe}$, $\text{HONH}_2\cdot\text{HCl}$	15
$\text{R}_3\text{SnCHR}'\text{CO}_2\text{R}^2$	R_3SnCl , $\text{NaCHR}'\text{CO}_2\text{R}^2$	16, 17
$\text{R}_2\text{Sn}(\text{CHR}'\text{CO}_2\text{R}^2)_2$	R_2SnCl_2 , $\text{NaCHR}'\text{CO}_2\text{R}^2$	16, 17
$\text{X}_2\text{Sn}(\text{CH}_2\text{CO}_2\text{R})_2$ (X = Br or I)	$\text{XCH}_2\text{CO}_2\text{R}$, Sn/Cu	18, 19
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{R}$ (R = H, alkyl, aryl)	SnCl_2 , HCl , $\text{CH}_2=\text{CHCO}_2\text{R}$	9
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$	Sn , HCl , $\text{CH}_2=\text{CHCO}_2\text{R}$	9
		(i) Me_3SnLi (ii) MeI 20
		(i) Me_3SnLi (ii) H_3O^+ 20
$\text{Me}_7\text{RSnCHR}^2\text{CHR}'\text{CO}_2\text{Me}$ (R = Cl, Me)	Me_7RSnH , $\text{CHR}^2=\text{CR}'\text{CO}_2\text{Me}$	21
$\text{R}_3\text{Sn}(\text{CH}_2)_2\text{COR}'$	R_3SnH , $\text{CH}_2=\text{CHCO}_2\text{R}$	22, 23
$\text{Ph}_3\text{Sn}(\text{CH}_2)_3\text{COR}'$	(a) Ph_3SnH , $\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{R}'$	6
$\text{Ph}_3\text{Sn}(\text{CH}_2)_4\text{COR}'$	(b) Ph_3SnNa , $\text{Br}(\text{CH}_2)_3\text{CO}_2\text{R}'$	20, 24
	(a) Ph_3SnH , $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{R}'$	5
	(b) Ph_3SnNa , $\text{Br}(\text{CH}_2)_4\text{CO}_2\text{Et}$	20
$\text{Me}_3\text{Sn}(\text{CH}_2)_3\text{CO}_2\text{H}$	$\text{Me}_3\text{Sn}(\text{CH}_2)_3\text{Br}$, (i) Mg	26
	(ii) CO_2	
$\text{Ph}_3\text{Sn}(\text{CH}_2)_3\text{CO}_2\text{H}$	$\text{Ph}_3\text{Sn}(\text{CH}_2)_3\text{CN}$, NaOH	25
$\text{Ph}_3\text{Sn}(\text{CH}_2)_4\text{CO}_2\text{H}$	Ph_3SnH (i) $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{Me}$	6
	(ii) NaOH	
$\text{Ph}_3\text{SnCH}_2\text{CONEt}_2$	Ph_3SnCl , $\text{BrZnCH}_2\text{CONEt}_2$	27
$\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{CONH}_2$	Ph_3SnH , $\text{CH}_2=\text{CHCONH}_2$	13
$\text{Ph}_3\text{SnCH}(\text{COR})_2$ (R = Me, OEt)	$\text{Hg}[\text{CH}(\text{COR})_2]_2$, $(\text{Ph}_3\text{Sn})_2\text{S}$	19

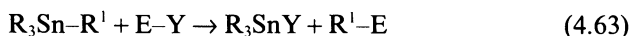
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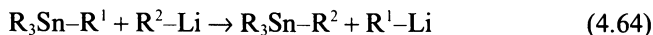
4.2 Cleavage of carbon-tin bonds [1, 23, 73, 127-130]

4.2.1 General aspects

Tin-carbon bonds may be cleaved in both heterolytic and homolytic processes. For heterolytic processes, electrophilic attack at carbon is usually the more significant, although nucleophilic assistance at tin can also aid the cleavage reaction and can even dominate (eqn 4.63).



Cleavages have been reported to occur with basic nucleophilic reagents, such as alcoholic alkali, alkoxide or alkali (e.g. with pentafluorophenyl- [131], aryl- [132], benzyl- [133], allyl- [134] and alkynyltin [135] compounds) and alkyl- or phenyllithium (with allyl-, vinyl- and α -functionally substituted alkyltin compounds (eqn 4.64) [27, 128].



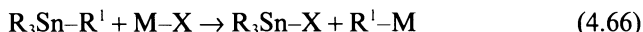
where R^1 = allyl, vinyl or XCH_2 ($\text{X} = \text{R}^3\text{O}$, R^3_2N , R^3S , etc.).

Cleavage by electrophiles. Among the various electrophilic reagents to react with a wide range of tin-carbon bonds are halogens, proton acids (e.g. hydrogen halides and carboxylic acids), metal(loid) halides (e.g. SnX_4 , HgX_2 , BX_3 , PX_5 , platinum and palladium halides, etc.) and sulphur dioxide. These reactions are used both for the synthesis of the organotin product, $\text{R}_n\text{SnY}_{4-n}$ (especially Y = halide or carboxylate) and the organic product, R^1-E . Cleavage of more than one carbon-tin bond can be brought about.

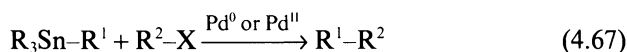
The disproportionation reaction of tin tetrahalides and organotin compounds, the Kocheskov reaction, has had extensive preparative use for both alkyl and aryl derivatives, e.g. eqn 4.65.



The mercury halide reactions, on the other hand, have been studied primarily for mechanistic purposes. These metal halide (MX) reactions show organotins acting as alkylating/aryllating agents (eqn 4.66).



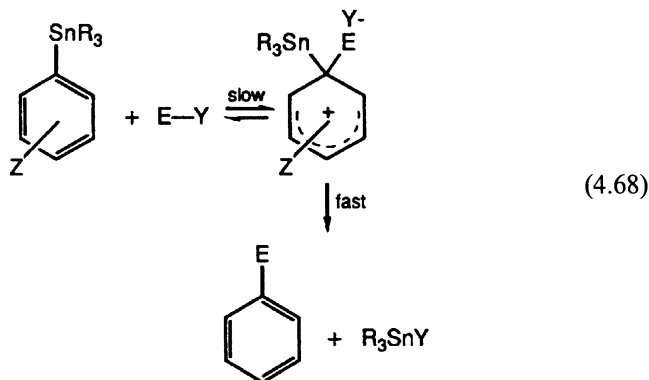
Organotins can also transfer organic groups to electrophilic carbon in transition metal-catalysed cross-coupling reactions with organic halides or esters, e.g. eqn 4.67.



Halogens can react via homolytic reactions (e.g. in light and in non-polar solvents) as well as by heterolytic routes (i.e. in the dark and in polar solvents). The reaction type may be of little consequence to the products of the reaction, but would have an impact on the stereochemistry of the reaction and on relative reactivities.

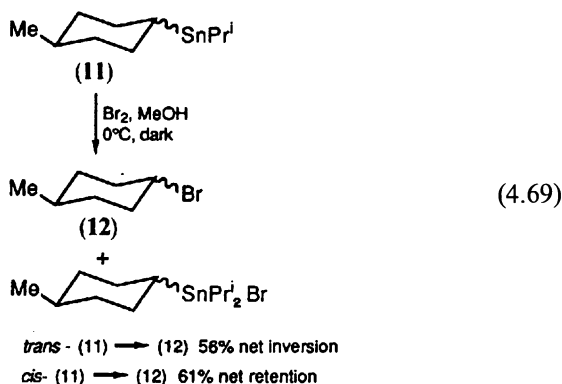
Many of the reactive electrophiles have only limited use and can be classed as being more of exotic than of either mechanistic or synthetic importance. The reactivity sequence for tin-carbon bonds in electrophilic cleavage reactions is generally allyl > phenyl > benzyl > vinyl > methyl > higher alkyl. The sequences for alkyltin bonds depend on the solvent and electrophile, and considerable variations have been realized.

Aryltin cleavages by electrophilic reagents are typical electrophilic aromatic substitutions [136, 137] with greater electron-releasing substituents, (Z), leading to faster reaction. Cleavage of Ar-Sn bonds provides Ar-E regioselectively (eqn 4.68) [128], e.g. Ar-F (using FOSO_4^- , Cs^+ [138], F-OAc or F_2 [139]); Ar-NO, from [140] NO-Cl; and Ar-D, from [128, 141] D-Cl,



D-O₂CCH₃, D-O₂CCF₃, etc. Other isotopically labelled groups *E* have been incorporated into aromatic groups via aryltin substrates [128]. Brominations, iodinations and protonolysis are the best studied reactions with regard to the kinetics and mechanism of aryltin bond cleavages.

Electrophilic cleavages of alkyltin bonds [130, 142, 143] are usually S_E2 processes. Here too, brominations and protonolysis dominate the kinetic-mechanistic studies. The findings up to the early 1970s have been well reviewed [1, 127, 142]. In subsequent work, more attention has been paid to the stereochemistry. For halogenations (I₂ and Br₂) [144-147], both net retention and inversion of configuration have been observed (eqn 4.69):



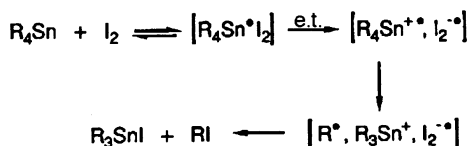
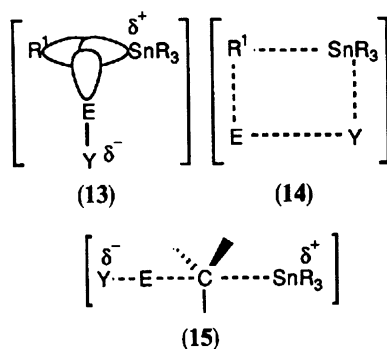
Three transition states have been considered [143]: (13), (14) and (15). Transition states (13) and (14) will lead to retention of configuration, with inversion arising from (15). Solvent, electronic effects and steric factors all play significant roles in determining the relative importance of these transition states and hence the overall stereochemistry.

In contrast to the electrophilic halogenations, shown in eqn 4.69, homolytic reactions of (11) with Br₂ in PhCl at 20°C in light gave (12) with no preferred stereochemistry. The stereochemical results for organotin compounds (e.g. eqn 4.69) contrast with the retention normally obtained for halogenations of dialkylmercurials.

An alternative view of halogenations of tetraalkyltins has been presented by Kochi [148]. In this approach, the rate-determining step is considered to be an electron transfer from a tetraalkyltin-halogen charge transfer complex (Scheme 4.13).

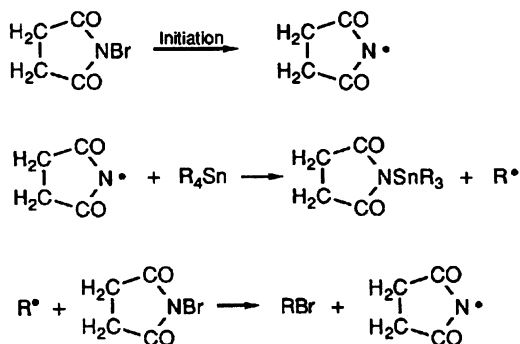
For protonolysis of alkyltins, retention of configuration is frequently obtained, e.g. reactions of trifluoroacetic acid with cyclohexyl(triisopropyl)stannanes occur stereospecifically with retention of configuration.

Homolytic cleavages [23, 149, 150]. Homolytic cleavage of a tin-carbon bond in a tetraorganotin is less common than is heterolytic cleavage. Examples of free radicals which have been shown to take part in S_H2



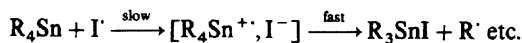
Scheme 4.13

displacement at the tin centre are Br^\bullet , I^\bullet and the succinimidyl radical (Scheme 4.14). Apparently, organotin halides react more readily by this mechanism. The reactivity found for R_4Sn in Me_2CO towards the succinimidyl radicals (*viz* $\text{Me} > \text{Et} > \text{Pr} \approx \text{Bu} > \text{Bu}^\bullet$) [151] is the reverse of that found for free radical reactions of I_2 or Br_2 . The sequence obtained [152] for free radical iodination of $\text{Me}_n\text{SnR}_{4-n}$ is $\text{Bu}^\bullet > \text{Pr}^\bullet > \text{Et} > \text{Pr}''$.



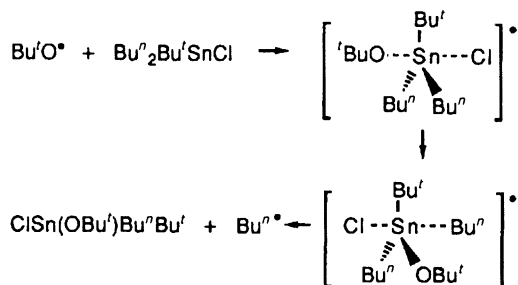
Scheme 4.14

An electron transfer mechanism has also been proposed for free radical iodination [152] (Scheme 4.15), and a similar mechanism was suggested [153, 154] for the photochemical-induced reaction between I_2 and R_3SnI .



Scheme 4.15

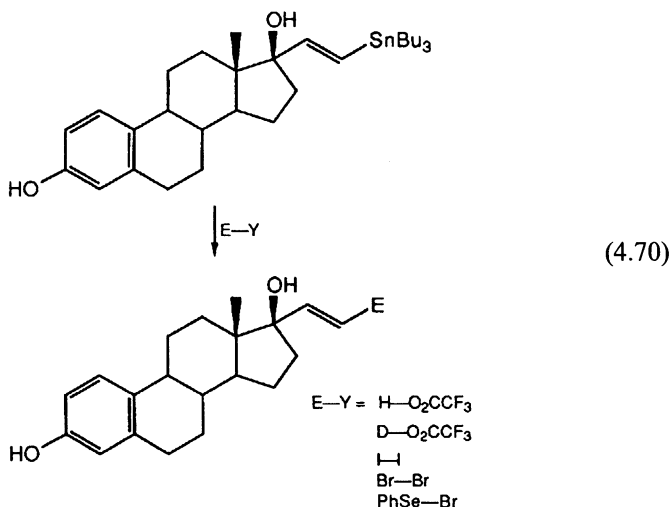
Alkoxy radicals attack the α - and β -carbon atoms of tetraalkyltins [155, 156]. In contrast, S_H2 reactions occur [157] at tin for trialkyltin compounds (Scheme 4.16).



Scheme 4.16

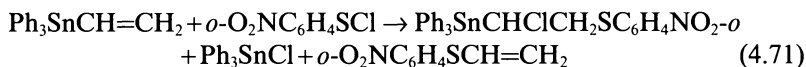
4.2.2 Reactions of specific groups [128]

Vinylstannanes. Vinyltin bonds are cleaved, with retention of configuration, by a variety of electrophilic reagents including proton acids [158, 159], halogens [159, 160] (e.g. I_2 in MeOH), mercury(II) halides [161], sulphur dioxide [162] and phenylselenyl bromide [160] (eqn 4.70).



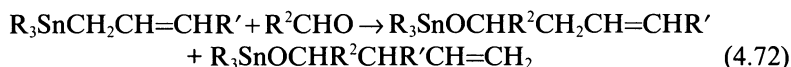
Reactions of $\text{Ph}_3\text{SnCH}=\text{CH}_2$ with electrophiles, such as I_2 , usually result in $\text{Ph}-\text{Sn}$ bond cleavage. However, sulphenyl halides react at the vinyl group, either resulting in addition to the vinyl group and/or cleavage of the vinyltin bond, e.g. eqn 4.71. Only the Markownikov adduct was isolated, which slowly decomposed in solution to Ph_3SnCl and $\text{CH}_2=\text{CHSC}_6\text{H}_4\text{NO}_2-o$. The relative proportions of cleavage to Markownikov addition varied with the

sulphenyl halides [163]. Other reagents, e.g. thiols, hydrogen sulphides, $\text{Cl}_3\text{C}-\text{X}$ ($\text{X}=\text{Cl}$ or Br) and perfluoroalkyl iodides, add to the vinyl groups of vinyltins in homolytic reactions [1, 127]. Epoxidation [164] and polymerization of vinyltins also results.

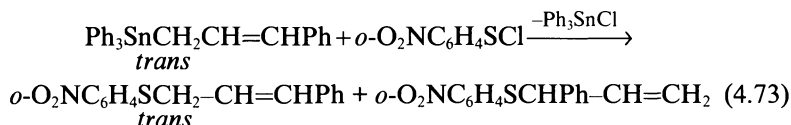


Transmetallations between vinyltins and organolithiums occur with retention of configuration.

Allylstannanes. Allyltin bonds are among the most reactive carbon–tin bonds; cleavage reactions occur with even mild electrophiles, such as carbonyl compounds, (eqn 4.72).

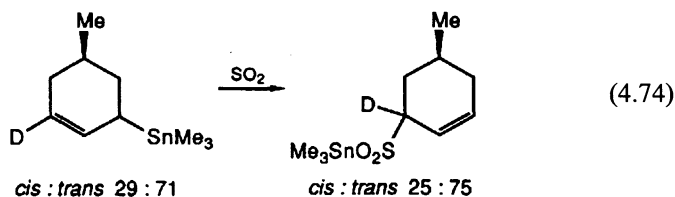


Both unrearranged and rearranged allylic products arise (eqns 4.72 and 4.73) [165].

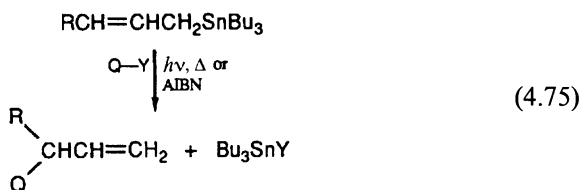


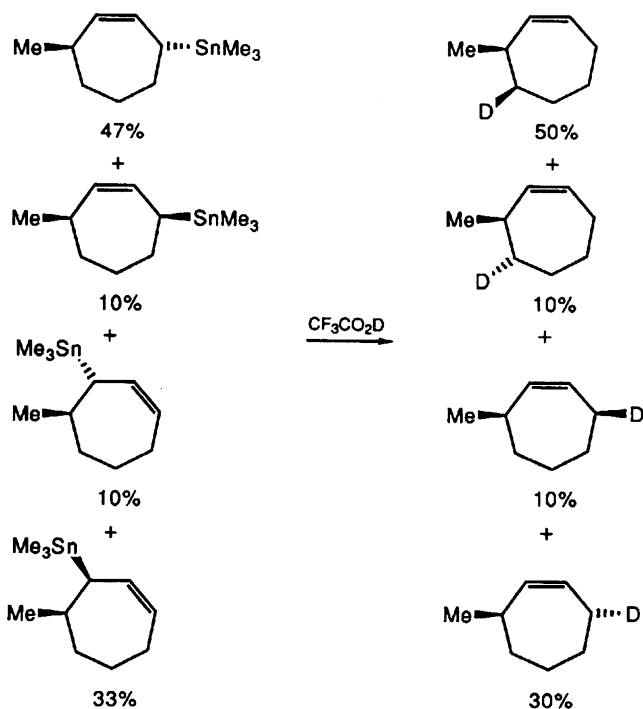
Protonolyses of allyltin bonds have been found to occur γ -regio- and anti-stereospecifically [128, 166–169], e.g. Scheme 4.17.

Sulphur dioxide reactions with allyltin compounds are also γ -regiospecific but exhibit *syn* stereospecificity (eqn 4.74) [168, 170].



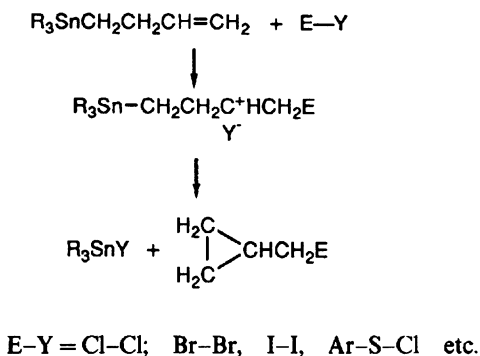
Hydrogen sulphide adds to the double bond in allyltin derivatives on UV irradiation at -78°C [171]. Other homolytic reactions of allylstannanes lead to cleavage, e.g. by $\text{RS}-\text{SR}$, $\text{PhSe}-\text{SePh}$, RSO_2-Cl and $\text{R}-\text{X}$ ($\text{Q}-\text{Y}$) (eqn 4.75) [128, 172].





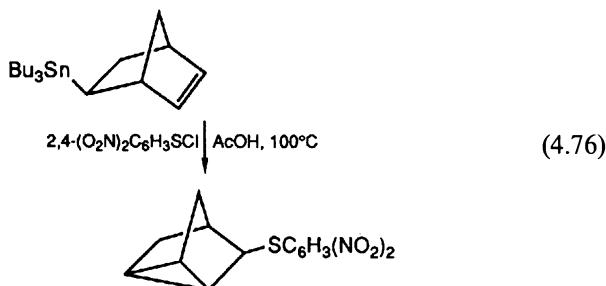
Scheme 4.17

3-Butenylstannanes. Reactions of 3-butenylstannanes with many electrophilic reagents result in carbon-tin bond cleavage and formation of cyclopropylmethyl derivatives (Scheme 4.18) [173, 174]. In contrast, an adduct, $\text{Ph}_3\text{SnCH}_2\text{CHCHClCH}_2\text{SC}_6\text{H}_4\text{NO}_2\text{-}o$, was isolated from the interaction of $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ with $o\text{-O}_2\text{NC}_6\text{H}_4\text{SnCl}$ at room temperature [175].

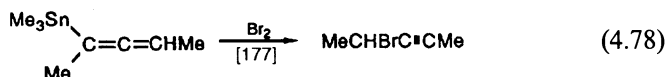
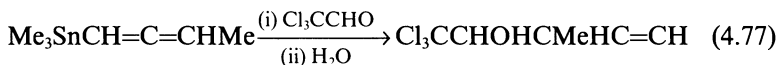


Scheme 4.18

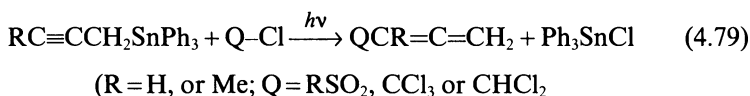
More vigorous conditions can, however, lead to elimination in nitrobenzenesulphenyl chloride reactions [174], as shown in eqn 4.76.



Propargyl- and allenylstannanes. Propargyl- and allenyltin bonds are reactive bonds, and cleavage reactions occur with many electrophilic species, including carbonyl compounds (eqn 4.77) [128, 176]. Reactions proceed with complete rearrangement for substituted derivatives (e.g. eqns 4.77 and 4.78) while unsubstituted species provide equilibrium mixtures of allenyl-propargyl derivatives.



Propargyltriphenylstannanes undergo $S_{\text{H}}2'$ substitution reactions with sulphonyl chlorides or polychloromethanes, alkyl bromides or iodides under UV irradiation or AIBN initiation, e.g. eqn 4.79 [172, 178].



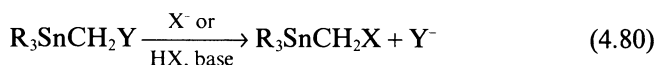
Functionally substituted alkylstannanes. A functional substituent in an alkyltin derivative can affect the reactivity of carbon-tin bonds and the type of reaction undergone. For example, in compounds of the type $\text{X}(\text{CH}_2)_n\text{-SnR}_3$, the substituent X can not only affect the reactivity of the $\text{X}(\text{CH}_2)_n\text{-Sn}$ bond (e.g. by its electronic influence) but also that of the Sn-R bond (e.g. by nucleophilic assistance by X at the tin centre). Reaction can also occur at X and lead to such processes as reduction, oxidation, 'onium salt formation and substitution without Sn-C bond cleavage, as well as leading to cleavage (via β or γ elimination) reactions of the Sn-(CH₂)_nX bond.

When a strongly electron-withdrawing group X is at the α -carbon, cleavage of that tin-carbon bond is greatly facilitated. Cleavages of Sn-CH₂X (X = COR, CO₂R, CN, etc.) occur readily with both basic nucleophiles and various electrophiles [75], including aldehydes [179]. Reactions of

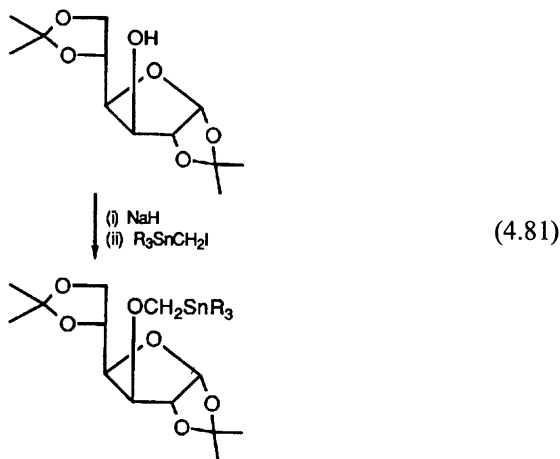
such $\text{Sn-CH}_2\text{X}$ bonds occur much more readily than those of simple alkyltin bonds, e.g. as shown by halogens and proton acids.

α -Substituents such as COR, CO_2R and CN stabilize the partial negative charge on carbon in the transition state leading to heterolytic cleavage. α -Sulphido groups also stabilize carbonic centres, and electrophilic cleavage of $\text{Sn-CH}_2\text{SR}'$ bonds occurs more readily than that of simple alkyltin bonds [180], as shown by reactions of $\text{Me}_3\text{SnCH}_2\text{SR}$ with HCl, HgCl_2 and halogens, which occur exclusively at the $\text{Sn-CH}_2\text{SR}$ bond. Reactions of $\text{Ph}_3\text{SnCH}_2\text{SR}$ (and $\text{Ph}_3\text{SnCH}_2\text{SeR}$) can take place at either or both tin-carbon bonds [180].

Generally for α -substituents (X), which are only weakly electron-withdrawing or are electron-releasing groups, there is less tendency for the $\text{Sn-CH}_2\text{Y}$ bond to be cleaved, although $\text{Sn-CH}_2\text{OR}$, $\text{Sn-CH}_2\text{NR}_2$, $\text{Sn-CH}_2\text{SR}$ and $\text{Sn-CH}_2\text{SeR}$ bonds are all readily cleaved by organolithium reagents. Substitutions can occur at the Y group, e.g. eqns 4.80 and 4.81. Ammonium salts have also been generated [177, 181] (eqn 4.82).



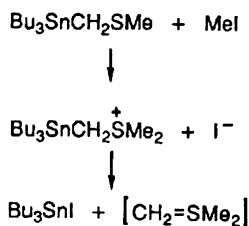
(Y = halide, X^- = halide [182], NR_2^+ , SR^+ , OR^+ or SeR^+ [183])



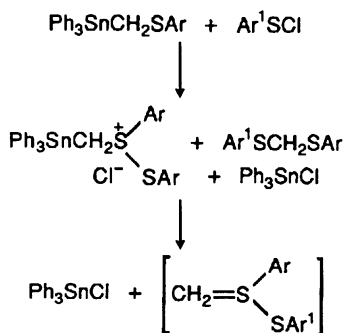
α -Haloalkyltins also can be used to form the corresponding Grignard and lithium reagents.

Initial attack at the substituent, Y, can lead to subsequent cleavage of the $\text{Sn-CH}_2\text{X}$ bond. Two examples from α -sulphide substituents [184] are shown in Schemes 4.19 and 4.20, in which intermediate sulphonium salts undergo reaction at the tin centre by the halide ions.

Electron-withdrawing groups (X) such as $\text{X}=\text{COR}$, CO_2R and CN, in β or

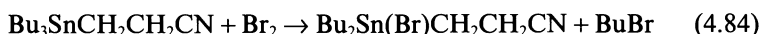
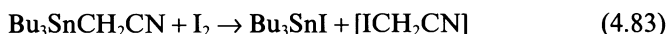


Scheme 4.19

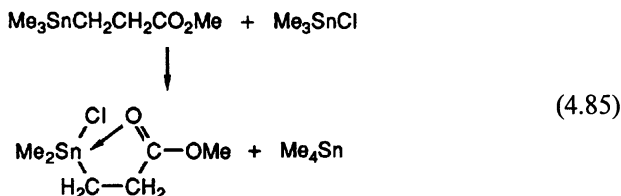


Scheme 4.20

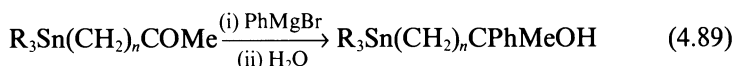
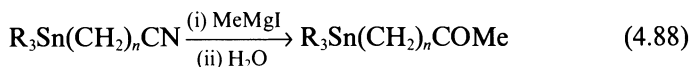
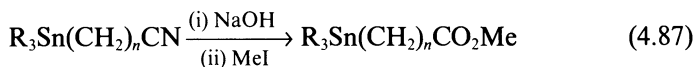
more remote sites, as a consequence of their decreased electronic effects at the carbon–tin bond, have no influence on the reactivity of the $\text{Sn}-(\text{CH}_2)_n\text{X}$ bond; compare eqns 4.83 and 4.84 [75, 180].



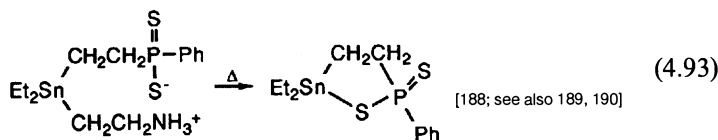
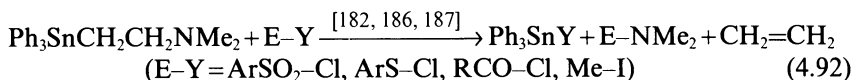
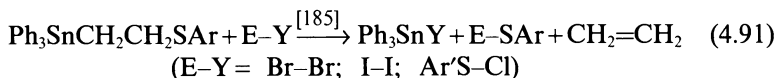
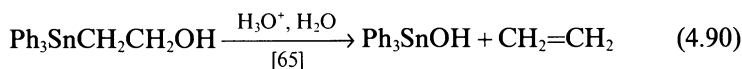
However, such β -substituents can affect the reactivity of the other carbon–tin bonds as a consequence of nucleophilic assistance (e.g. eqn 4.85). The nucleophilic assistance of the $\text{C}=\text{O}$ group in the transition state of the cleavage reaction renders it possible for the methyl–tin bond to be cleaved by such a weakly electrophilic reagent as Me_3SnCl [78].



Reactions of $\text{R}_3\text{Sn}(\text{CH}_2)_n\text{Y}$ ($n > 2$; $\text{Y} = \text{COR}$, CO_2R or CN) do occur with nucleophiles or basic reagents, e.g. reduction using LiAlH_4 , hydrolysis by NaOH and alkylations using Grignard reagents, e.g. eqns 4.86–4.89 [75] (see also Tables 4.2 and 4.7).



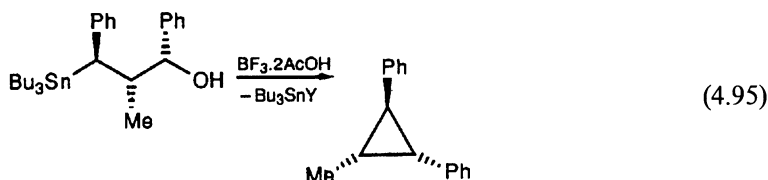
Organotin compounds containing such β -substituents as OH, OR, SR, NR_2 or PR_2 , undergo ready β -eliminations on reaction with certain electrophiles or on thermolysis, and examples are shown in eqns 4.90–4.93. 2-Acetoxyvinyl compounds eliminate acetylene on heating, with the triphenyltin derivative being more thermally stable than is the methyl analogue [75].



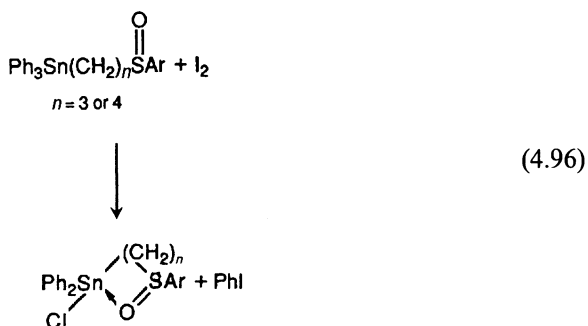
Alkene elimination can also occur on treatment of alkyltins, bearing β -hydrogens, for example on reaction with the hydride-abstracting agent Ph_3C^+ , BF_4^- [191, 192] (eqn 4.94), which proceeds by *trans*-elimination.



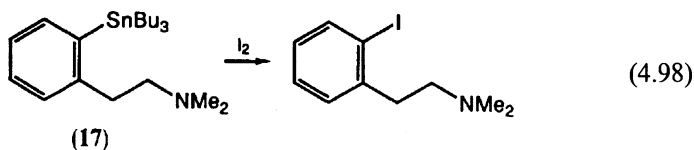
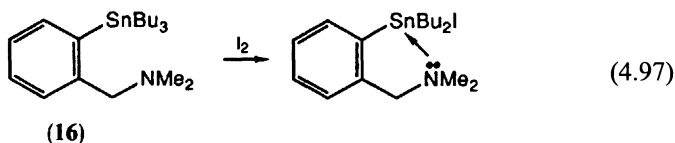
Substituents in positions more remote than β from tin in $\text{R}_3\text{Sn}-(\text{CH}_2)_n\text{Y}$ do not influence the reactivity of the $\text{Sn}-(\text{CH}_2)_n\text{Y}$ bond unless γ -eliminations are possible. γ -Hydroxyalkyltin compounds undergo interesting stereospecific eliminations to give cyclopropanes on treatment with acids [193], e.g. eqn 4.95, or with thionyl chloride [194].



As already pointed out (e.g. eqn 4.85) substituents in one bond can increase the reactivity of the remaining R-Sn bonds (by nucleophilic assistance). The remote substituents Y can of course undergo their usual substitution, addition, oxidation or reduction chemistry, providing the reagents necessary for such reactions do not also react at tin-carbon bonds. Nucleophilic assistance has been found in a number of reactions, including reactions of $\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{S}(\text{O})_m\text{Ar}$ ($n=2, 3$ or 4 ; $m=0, 1$ or 2) with iodine. In particular, strong nucleophilic assistance was established for sulphoxide groups [195] eqn 4.96.



Quite dramatic changes in reactivities have been observed [196] due to intramolecular nucleophilic assistance, including examples where alkyltin bonds are cleaved in preference to aryl- or vinyltin bonds, e.g. eqn 4.97 (cf. eqn 4.98).



The potential chelate ring (six-membered) from (17) is less strong than that formed from (16) (a five-membered ring), and the usual reactivity sequence of aryltin > alkyltin is found.

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5 Organometallic compounds of tetravalent tin

KIERAN C. MOLLOY

5.1 Introduction

Over the last 30 years, research into the chemistry of organometallic compounds of tin in the +4 oxidation state has represented one of the most prolific areas of chemical activity. As a result of the serendipitous coupling of an arsenal of sophisticated analytical techniques (Chapters 13 and 14) and widespread industrial applications (Chapter 12) the many facets of this field have attracted the attention of chemists of all persuasions, as well as that of biochemists, biologists, pharmacologists, toxicologists and physicists, to name but a few. The reader's attention is drawn to existing books [1–3], review articles [4,5] and periodic surveys [6] covering this field. Invaluable databases relating to studies of organotin compounds by NMR [7–10] and Mössbauer spectroscopies [11, 12] and single crystal X-ray diffraction [13, 14] also provide an entry into both structural and synthetic aspects of organotin chemistry.

5.2 Introducing reactivity: synthetic precursors to functionalized organotin (IV) compounds

Tetraorganotin compounds are usually colourless solids or oils, thermally stable at $<200^{\circ}\text{C}$, and are stable in moist air, although some recently prepared *C*-organostannyl heterocycles are unusually aerobically sensitive [15]. Preparative and physical data for both symmetrical and unsymmetrical tetraorganotin compounds are contained in three volumes of the Gmelin series, covering literature up to 1975 [16–18]. The formation and cleavage reactions of the Sn–C bond are described in Chapter 4.

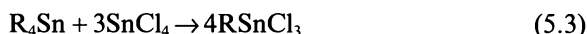
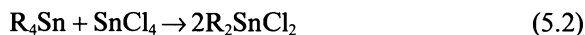
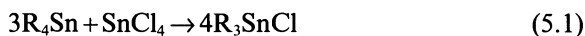
Unlike most metal–carbon bonds the Sn–C bond is of low polarity and hence is relatively unreactive. The stability of the Sn–C bond is largely responsible for both the extent and nature of the commercial utility of organotin compounds, but while R_3Al compounds for example are active olefin polymerization catalysts due to the highly polar Al–C bonds, R_4Sn compounds are too unreactive to be of significant importance save as precursors for less alkyl- or arylated species. Reactivity is introduced into an organotin moiety usually via tetraorganotins, by replacing Sn–C by more polar (e.g. Sn–Cl or Sn–O), or thermodynamically weaker (e.g. Sn–Sn) link-

ages. These compounds provide the synthetic base on which all organotin(IV) chemistry rests.

5.2.1 Organotin(IV) halides

The single most important class of organotin compounds embraces those species containing one or more tin–halogen bonds. These compounds have been comprehensively surveyed in four volumes of Gmelin [19–22]. Physical data for these compounds are given in Table 5.1. Organotin fluorides are generally only sparingly soluble in organic solvents due to their associated nature, while the other halides are readily soluble in organic solvents, and the methyltin compounds are also soluble in water. Organotin iodides are the least thermally stable of the series.

The classical preparation for these compounds is the Kocheshkov redistribution reaction between a tetraorganotin and a tin(IV) halide SnX_4 [23, 24]. Tin(IV) chloride is most commonly used, and, with the appropriate choice of reaction stoichiometry, mono-, di- or triorganotin halides can be made the dominant products.



Similar reactions proceed with unsymmetrical tetraorganotins:



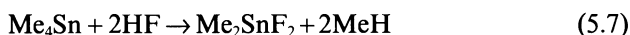
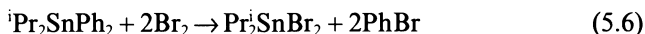
In addition to SnX_4 , a variety of other inorganic halides participate in this type of redistribution reaction, namely BCl_3 , AlCl_3 , SiCl_4 , GeCl_4 , BiCl_3 , TiCl_4 , and HgCl_2 , but are less commonly employed [25].

Both halogens and hydrogen halides cleave Sn–C bonds, and provide a

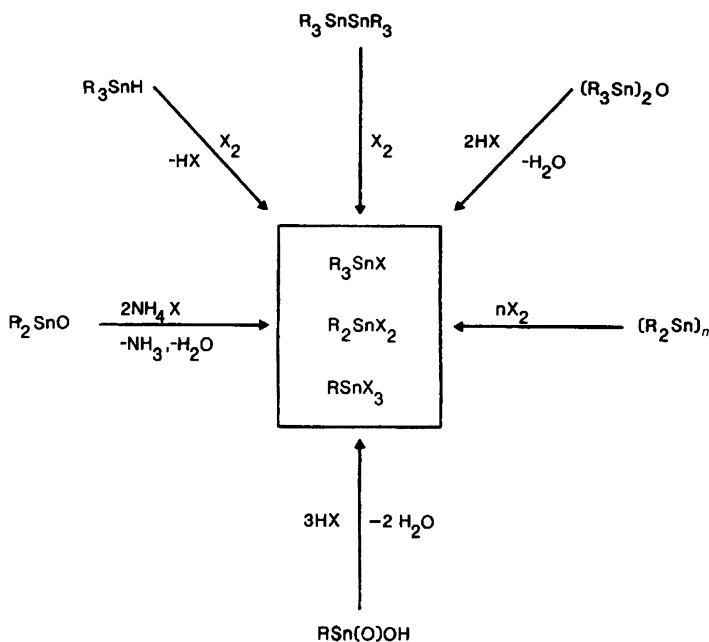
Table 5.1 Melting points ($^{\circ}\text{C}$) or boiling points ($^{\circ}\text{C mmHg}^{-1}$) for organotin halides, $\text{R}_n\text{SnX}_{4-n}$ [5]

R	n	X = F	Cl	Br	I
Me	3	375d	37–38	26–27	67–68/15
Me	2	>300	107–108	75–77	43–44
Me	1	321–327	45–46	55	85
Et	3	302	210/760	224/760	234/760
Et	2	310–320	84	63	44
Et	1	269–272	86/12	46/0.1	181–184.5/19
Bu	3	248–252	152–156/14	120–122/2	108/0.07
Bu	2	156–157	40–41	20(96/0.1)	145/6
Bu	1	337–338	93/10	77–79/0.2d	154/5
Ph	3	357d	105	124–125	122–124
Ph	2	>300	40–42	37	72–73
Ph	1	220	128/15	182–183/29	31–32

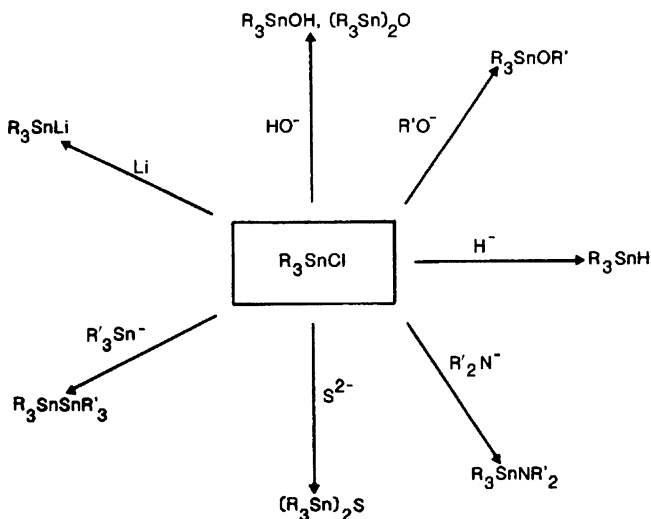
simple, economical way to form organotin halides. Unsymmetrical organotin halides are conveniently prepared in this way, since the relative ease of halide for hydrocarbon substitution broadly follows the stability of the leaving carbanion, viz: $\text{Ph} > \text{PhCH}_2 > \text{vinyl} > \text{Me} > \text{Et} > \text{Pr} > \text{Bu}$ [25]. Iodine is the reagent of choice for cleavage of only one $\text{Sn}-\text{C}$ bond, while Br_2 can substitute up to two organic groups depending upon stoichiometry and substrate. Typical examples are (Refs 26, 27; K.C. Molloy and P. Brown, unpublished results):



The above methods, in conjunction with the direct synthesis discussed in Chapter 4, are the most versatile and practical syntheses of organotin halides. Other Sn -halogen bond-forming reactions are shown in Scheme 5.1, but since the reagents are themselves usually derived from organotin halides they offer no advantages over conventional methods. Once formed, the Sn -halogen bond will undergo a wide range of nucleophilic substitution reactions, some of which are shown in Scheme 5.2 for the triorganotin series.



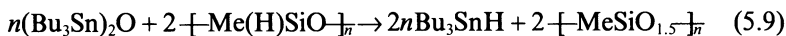
Scheme 5.1 Formation of organotin-halogen bonds ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).



Scheme 5.2 Nucleophilic substitution reactions of triorganotin halides.

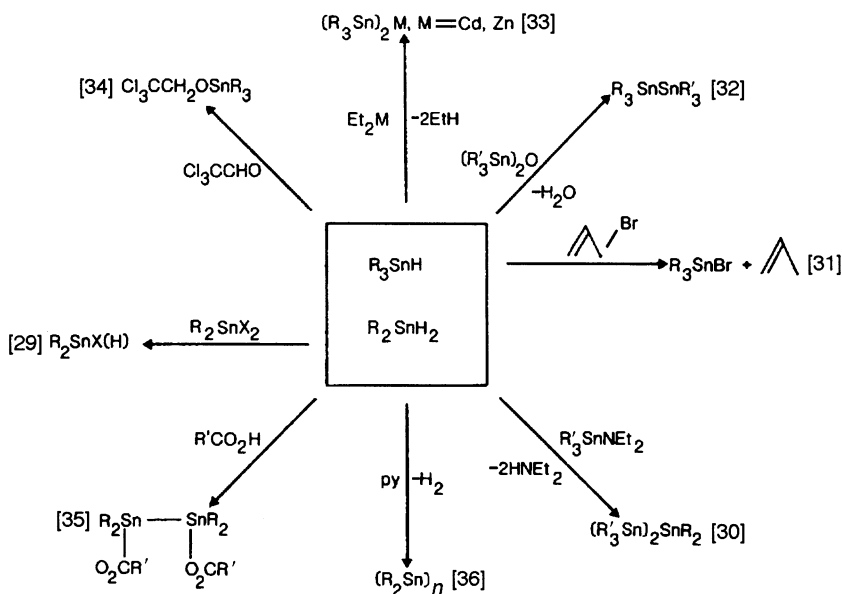
5.2.2 Organotin(IV) hydrides

Organotin halides and oxides can be reduced by either LiAlH_4 or poly(methylhydrosiloxane) to yield organotin hydrides:



For common alkyl- and aryltins the products are distillable liquids, whose instability in air and towards heat increases as the number of organic groups decreases. These compounds have been reviewed as part of the Gmelin series [28], and are characterized spectroscopically by an absorption at $c. 1800 \text{ cm}^{-1}$ in the IR and $^1J(^{119}\text{Sn}-^1\text{H}) \sim 1500\text{--}2000 \text{ Hz}$ in their NMR spectra.

A variety of reactions for organotin hydrides are possible, depending largely on the mechanism of Sn-H bond cleavage. With weak nucleophiles, the organotin hydride will provide a source of nucleophilic hydrogen and exchange reactions result [29]. If a stronger nucleophilic centre such as NR_2 is present in the substrate, the Sn-H moiety releases electrophilic hydrogen, which is particularly useful in the formation of Sn-metal bonds [30]. Homolytic cleavage of the Sn-H bond yields organostannyl radicals which may undergo addition reactions with alkynes and alkenes (hydrostannation) or exchange reactions with alkyl halides (hydrostannolysis) [31]. Some typical reactions of organotin hydrides are shown in Scheme 5.3 [29–36]. Very little work has been carried out on the reactivity of organotin trihydrides, although the synthesis of stable solid compounds of this type incorporating



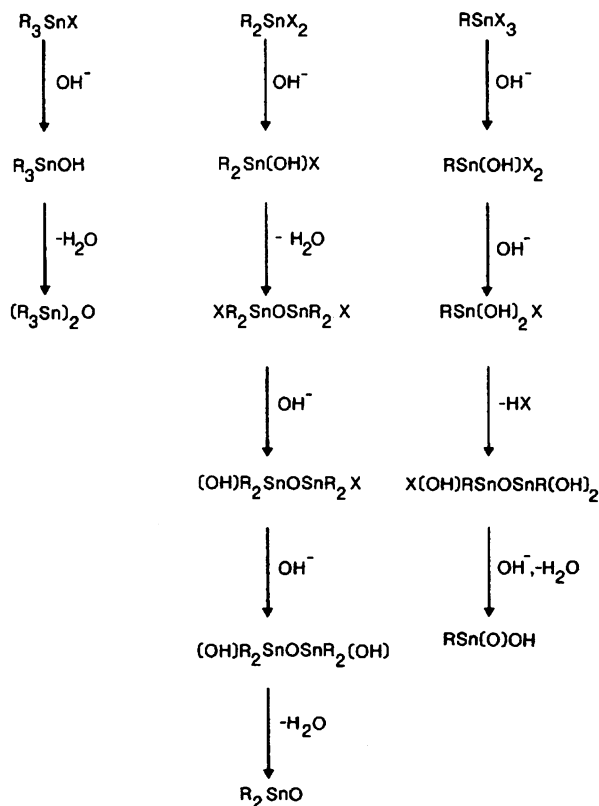
Scheme 5.3 Typical reactions of tri- and diorganotin hydrides.

sterically bulky organic groups such as $(\text{Me}_3\text{Si})_3\text{CSnH}_3$ [37] may promote interest in this area.

5.2.3 Organotin(IV) oxides, hydroxides and alkoxides

Base hydrolysis of organotin halides leads to a variety of organotin oxygen compounds (Scheme 5.4) which have a rich structural and synthetic chemistry. In addition, $(\text{Bu}_3\text{Sn})_2\text{O}$, Ph_3SnOH , Cy_3SnOH and $[(\text{Neophyl})_3\text{Sn}]_2\text{O}$ are commercial biocides.

The nature of the hydrolysis products increases in complexity with increasing halogen content of the precursor. Triorganotin halides yield initially hydroxides, which are stable where $\text{R} = \text{Me}$, aryl or bulky alkyl (e.g. cyclo- C_6H_{11}). Other triorganotin hydroxides spontaneously condense to the corresponding bis(triorganotin)oxides. In the diorganotin series, the 1,1,3,3-tetraorgano-1,3-dihalodistannoxanes and diorganotin oxides are well characterized, but other partial hydrolysis products have only been isolated in cases where steric bulk inhibits condensation reactions, e.g. $\text{Bu}_2\text{Sn}(\text{OH})\text{Cl}$ [38], $\text{ClPr}_2\text{SnOSnPr}_2\text{OH}$ [39] and $[(\text{OH})\text{Bu}'\text{Me}_3\text{SiCH}_2\text{Sn}]_2\text{O}$ [40]. Similarly, while most diorganotin oxides are amorphous, polymeric materials, several oligomeric oxides are now known, e.g. $[\text{Bu}_2\text{SnO}]_3$ [41]. Less attention has been paid to the hydrolysis products of organotin trihalides, although $\text{EtSn}(\text{OH})\text{Cl}_2 \cdot \text{H}_2\text{O}$ has been isolated as a hydroxy-bridged dimer [42]. The



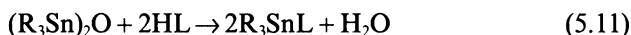
Scheme 5.4 Stepwise hydrolysis products of organotin halides (X = halogen).

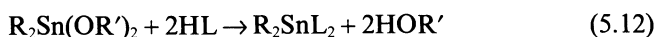
stannic acids, RSn(O)OH , are usually polymeric powders, but again bulky hydrocarbons yield soluble, presumably oligomeric, materials, e.g. $(\text{Me}_3\text{Si})_3\text{CSn(O)OH}$ [43].

Closely related to these systems from a synthetic viewpoint are the organotin alkoxides. These are prepared by nucleophilic substitution of Cl^- by RO^- within an organotin halide and, unlike the oxides/hydroxides, are often aerobically sensitive.



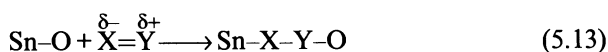
As synthetic precursors to other organotin compounds, synthons containing Sn–O bonds may be utilized in one of two reaction classes. The predominant class is heterolytic substitution, usually involving protic ligands. Reactions of the following general form are typical:





Reactions in which H_2O is the by-product are driven by its azeotropic removal using toluene as solvent. Carboxylic [44], oxy-sulphur [45–47], oxy- and thiophosphorus [48, 49], and nitric acids [50] make an arbitrary but representative list of ligands which form organotin esters by this route. Other examples of substitution reactions involving Sn–O bonded compounds are shown in Scheme 5.5 [32, 51–58].

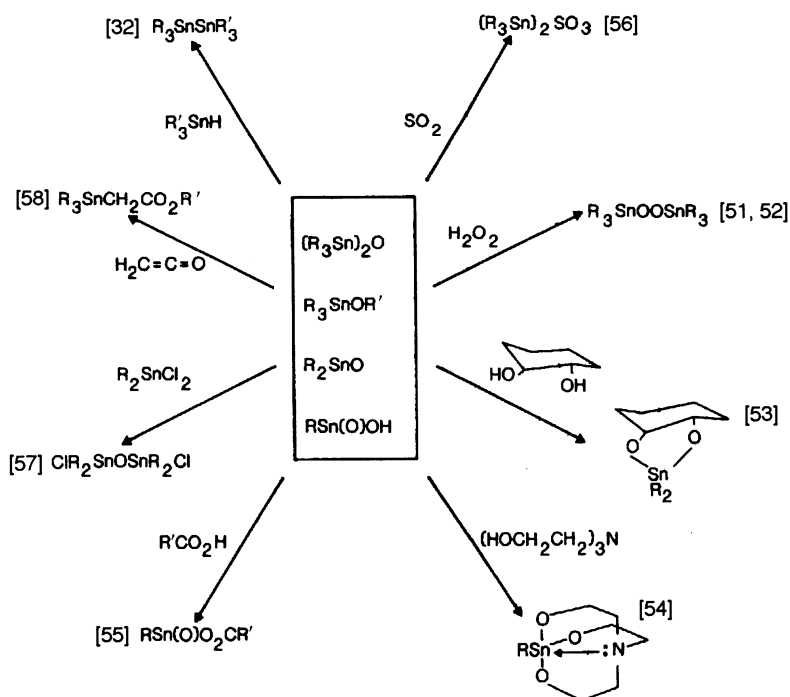
Also included in Scheme 5.5 are examples of a second reaction type, insertion into the polar Sn–O bond.



One of the more environmentally significant consequences of this type of reactivity is the conversion of the wood preservative $(\text{Bu}_3\text{Sn})_2\text{O}$ to $(\text{Bu}_3\text{Sn})_2\text{CO}_3$ within the cellulose structure [59].

5.2.4 Organotin(IV) amines

Amino-nucleophiles, usually as lithium but occasionally as other alkali

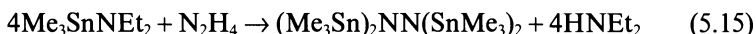


Scheme 5.5 Typical reactions of organotin–oxygen compounds.

metal, magnesium or organosilicon derivatives, displace Cl^- from organotin chlorides to yield organostannyl amines. For example [60]:



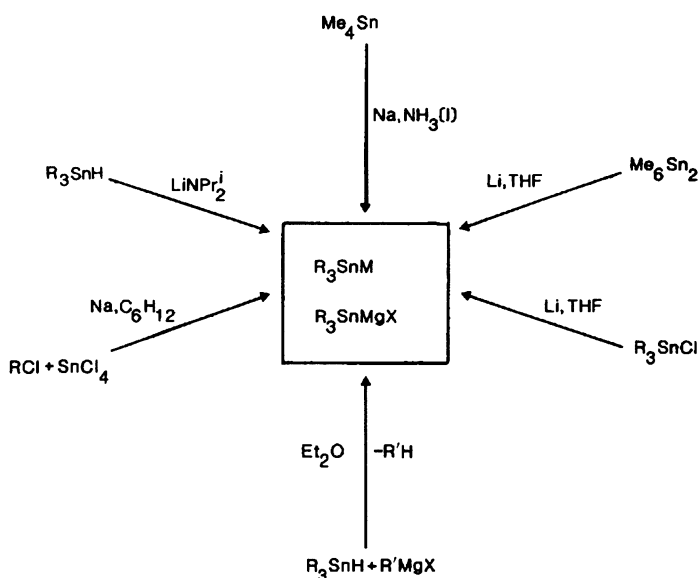
Derivatives of less volatile amines can then be synthesized by a transamination route [61]:



The Sn–N bond can be cleaved by even mildly protic ligands to form other organotin compounds, and the evolution of gaseous amine used to promote reaction. Insertion reactions are also known, and in each of these reaction types the Sn–N compounds are more reactive than their Sn–O counterparts.

5.2.5 Organostannyl anions

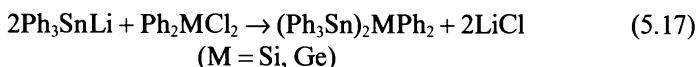
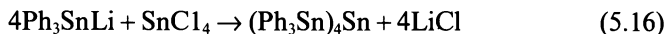
For practical purposes, organostannyl anions can be considered simply as their lithium or sodium salts, although magnesium derivatives are also of value. Organotin-copper reagents [62] R_3SnCuX have also found application in organic synthesis. Triorganostannyl anions have been considerably more widely exploited than R_2SnM_2 or RSnM_3 type species. The former class of compound can be prepared by the routes of Schemes 5.6, and their synthetic chemistry has been reviewed [63, 64].



Scheme 5.6 Formation of organostannyl anions.

Organotin nucleophiles will react with a variety of carbonium centres, such as alkyl halides [65], aldehydes, ketones and oxetanes [66, 67] to form Sn–C bonds. In the case of reactions with alkyl halides, the stereochemistry of the reaction is dependent on the nature of R, X, M and the solvent, and mechanisms such as S_N2 at C, S_N2 at X and radical pair have been suggested [64, 68].

Alternatively, organostannyl anions react with metal halides to form new Sn–metal bonds and this reaction type has been widely exploited, as exemplified by [69, 70]:



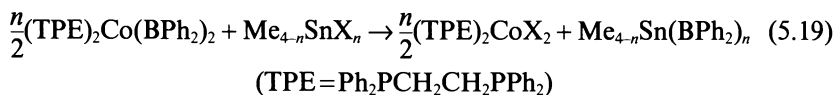
5.3 Construction and reactivity of Sn–element bonds

The synthesis of R_nSn –element bonds is covered systematically by group, except for the halogens whose chemistry has already been covered.

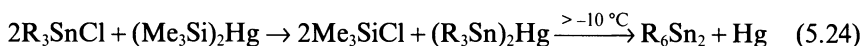
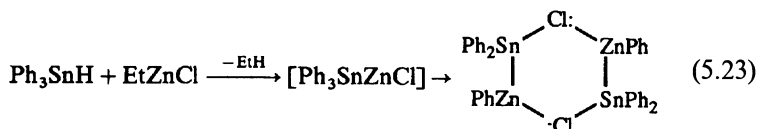
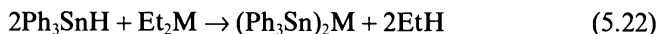
5.3.1 Groups 1, 2, 12 and 13

Apart from the Li, Na and Mg organostannyl anions, little attention has been paid to the derivatives of Groups 1 and 2. The solvent dependence of R_3SnM reactivity suggests that solvent coordination is an important structural component of these systems, but this is yet to be confirmed crystallographically. The structure of Ph_3SnK –18-crown-6 has been reported in which a pyramidal Ph_3Sn^- anion is 7600 pm from the nearest 18-crown-6 complexed K^+ cation [71] and tin can also be bonded directly to Li [213] or K [214]. R_2SnM_2 species have not been developed to the same extent as their triorganotin analogues, nor have systems based on the more electropositive of the Group 1 and 2 elements (Rb, Cs, Ca, Sr, Ba), though the Sn–Ca bond has now been characterized [215].

Organotin–boron compounds are better established [216], though these centre mainly on borane and carborane [217]. Four approaches have been reported, using both nucleophilic [72, 73] and electrophilic [74–76] boron reagents:



Equation 5.21 has also been applied to the more electropositive Group 3 elements using R_3M as Lewis acids, but the products appear to be quite unstable [176]. Several examples of Sn–M bonded compounds ($M = \text{Zn, Cd, Hg}$) are known, and their structures have been assigned, tentatively, on spectroscopic evidence [34, 77–80].

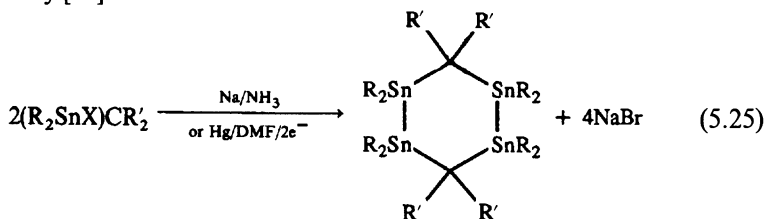


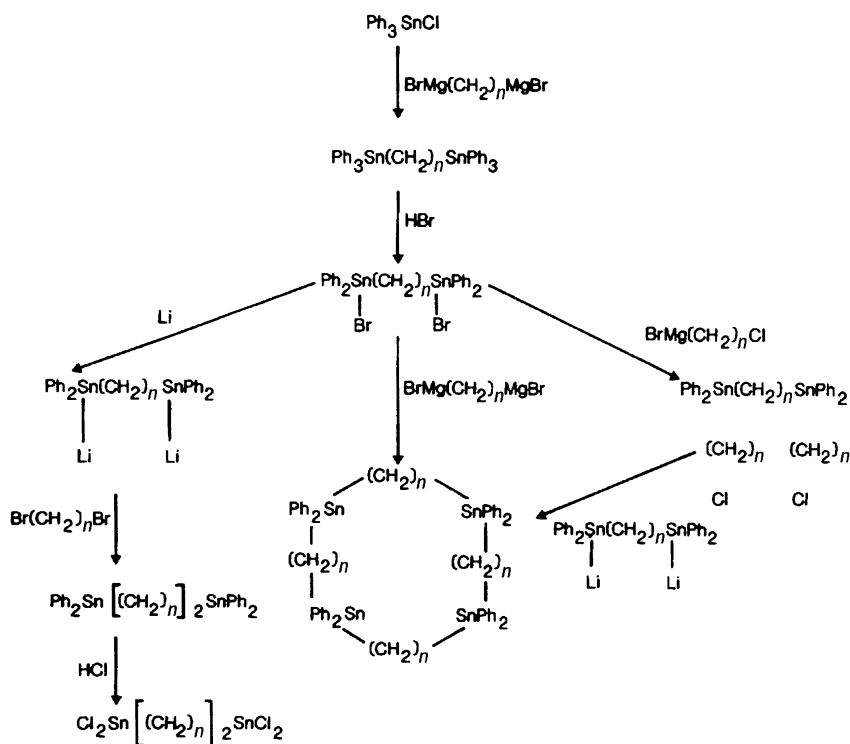
$(\text{R}_3\text{Sn})_2\text{Hg}$ species can also be synthesized by electrochemical methods [81]. The direct Sn–Hg bond is corroborated by the large one-bond $^1J(^{119}\text{Sn}-^{199}\text{Hg})$ coupling constant of ~ 6000 Hz [82].

5.3.2 Group 14

Although synthetic aspects of the Sn–C linkage have already been covered, one recent example from what is likely to be an expanding area of activity serves to underscore several features of the chemistry of this bond type. The Lewis acidity of tin makes it suitable for incorporation into macrocycles designed for anion binding, to complement the well established area of cation binding by basic host macrocycles, e.g. crown ethers. Scheme 5.7 outlines routes developed by Newcomb *et al.*, and elegantly demonstrates the use of lithium and Grignard reagents in Sn–C bond formation, and the selective cleavage of Sn–C(aryl) over Sn–C(alkyl) bonds to introduce reactivity. Macrocycles of architecture $n = 8, 10, 12$ all bind Cl^- ions strongly, and a small macrocycle selectivity effect exists in favour of the 18-ring ($n = 8$) species [83, 84].

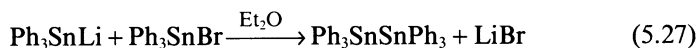
Synthesis of the basic skeletons of organic molecules which contain tin and other Group 14 elements in place of carbon continues to attract interest. Unfunctionalized polytin compounds can be prepared by coupling of triorganotin halides in the presence of metal, both chemically [85, 86] or electrochemically [87]:



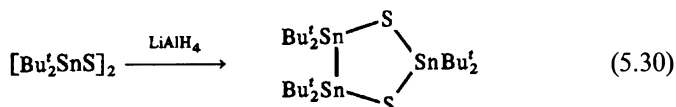
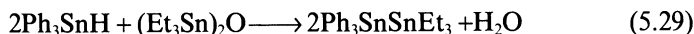
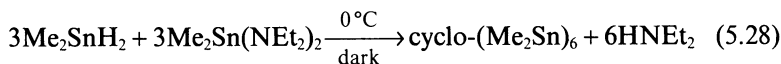


Scheme 5.7 Synthetic routes to polytin macrocyclic anion hosts.

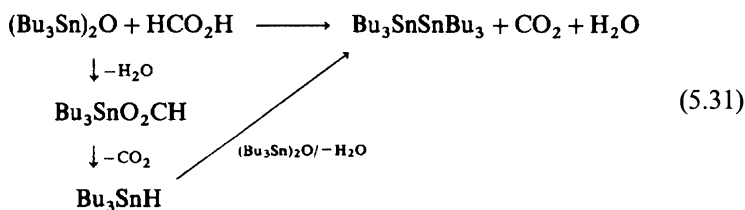
Preformed organostannyl anions may [88] also be used:



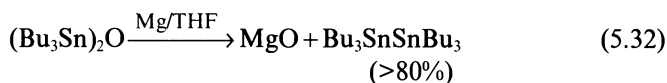
Alternatively, Sn–N [89], Sn–O [33] and Sn–S [90] bonds may be reduced by tin hydrides to yield Sn–Sn bonds:



Bis(triorganotin)oxides will also react with formic acid to yield ditin compounds in 40–70% yield, by a sequence which probably involves an organotin hydride [91]:



Magnesium along with other less convenient metals (Ti, Na, K), will also reduce $(\text{R}_3\text{Sn})_2\text{O}$ in good yield [92]:



The reaction of Grignard reagents with tin(II) halides also yields polytin compounds, whose Mössbauer isomer shift values ($\sim 1.55 \text{ mm s}^{-1}$) [93] characterize them as tin(IV) products:

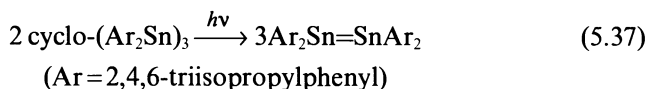


Tin-silicon, -germanium [94, 95] or -lead [96] bonds are prepared by methods similar to those described above and are illustrated by the following examples:

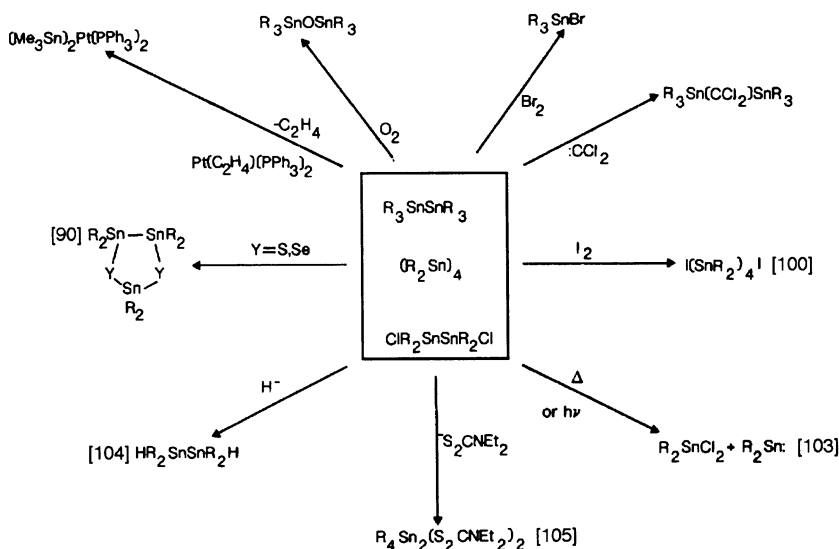


^{119}Sn chemical shifts are sensitive to the degree of chain branching in these systems, moving to higher field as tin is increasingly metallated from a primary to a quaternary centre [97].

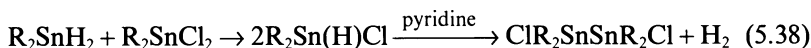
The reactive centre in compounds of type $\text{R}_3\text{SnMR}'_3$ ($\text{M} = \text{Si, Ge, Sn, Pb}$) and their cyclic or longer chain relatives is always the Sn-M bond. Some typical reactions are shown in Scheme 5.8 [5]. Of particular interest is the recent demonstration that cyclic polytin compounds can be photochemically converted to $\text{Sn}=\text{Sn}$ compounds [98].



Polytin compounds which incorporate other reactive centres, such as Sn-halogen bonds, have been less well investigated than the simple, unfunctionalized polyorganotins, although these compounds are precursors to a wide area of unexplored structural chemistry. Such compounds can be made by coupling of diorganotin (halogen)hydrides (eqn 5.38) [99], controlled opening of cyclic polytins by halogens (Scheme 5.8), [100] or electrochemical methods [101].



Scheme 5.8 Reactions of Sn-Sn bonded compounds.



$\text{ClMe}_2\text{SnSnMe}_2\text{Cl}$ has been shown to exist as a chlorine-bridged, double chain polymer [102]. Some reactions of this type of compound are shown in Scheme 5.8 [103–105].

The most thoroughly investigated reaction type is with bidentate ligands such as carboxylates, which span the Sn-Sn bond [105–108].

5.3.3 Group 15

Organotin amines of formulae $\text{R}_n\text{Sn}(\text{NR}'_2)_{4-n}$, $(\text{R}_3\text{Sn})_n\text{NR}'_{3-n}$ ($n=1, 2, 3$) and $(\text{R}_2\text{SnNR}')_n$ ($n=2, 3$) are known, and their chemistry has been reviewed [109, 110]. Preparation of these species by lithioamination and transamination methods has been described previously. The synthetic value of these compounds is the ease with which the Sn-N bond is cleaved by protic reagents, although this also renders these compounds sensitive to atmospheric moisture. The triorganotin amines are usually monomeric, but trimethyltin aziridine has been ascribed a polymeric structure on the basis of its Mössbauer quadrupole splitting (2.24 mm s^{-1}) and spectral area temperature-dependence data [111]. Triorganotin derivatives of imidazoles and triazoles [112, 113] are more stable than the simple amines, and these species form N-bridged polymeric structures. The structure of the acari-

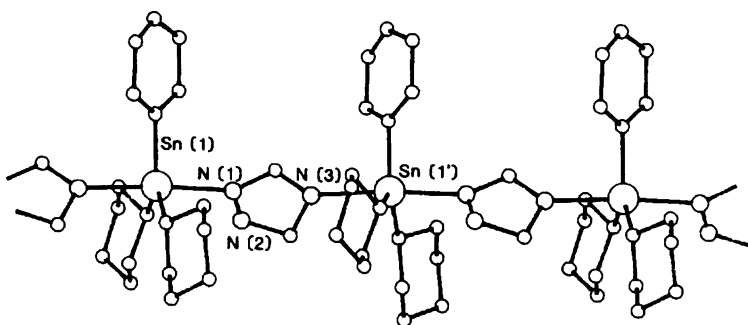
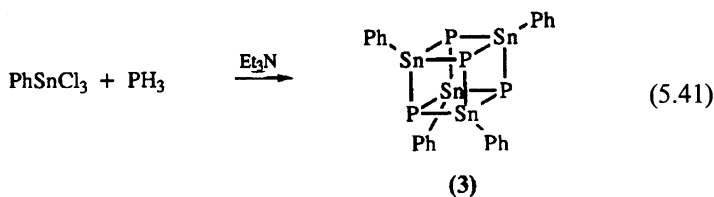
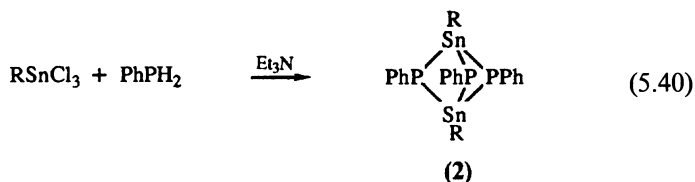
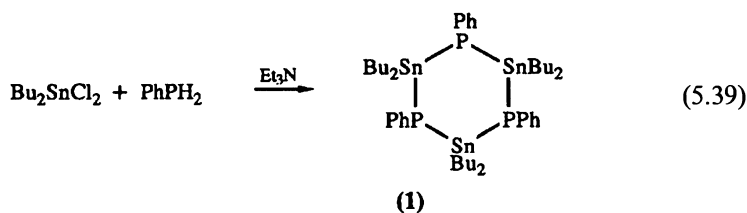


Figure 5.1 The structure of tricyclohexylstannyl-1,2,4-triazole. (Redrawn by permission from Ref. 114.)

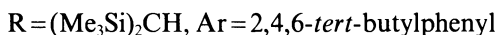
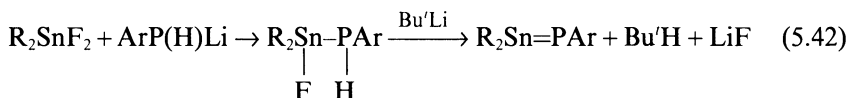
cidally active $\text{Cy}_3\text{Sn-1,2,4-triazole}$ is shown in Figure 5.1 [114]. In contrast, electron diffraction data show $(\text{Me}_3\text{Sn})_3\text{N}$ to have a planar $[\text{Sn}_3\text{N}]$ skeleton with an Sn–N bond length of 203.8 pm [115].

The bond between tin and the heavier Group 15 elements may be synthesized by similar means to the Sn–N bond. For phosphorus in particular, the use of polyfunctional reagents has led to a variety of ring and cage structures [116–118], although the products of eqns 5.39–5.41 await crystallographic verification.



When elemental phosphorus is reduced by the ditin dihydride $\text{Me}_4\text{Sn}_2\text{H}_2$, an unusual cage structure (Figure 5.2a) [119] results which is stable in the dark, but in sunlight eliminates dimethylstannylene, $\text{Me}_2\text{Sn:}$, to yield a norbornane type structure (Figure 5.2b) [120].

The first example of a $\text{Sn}=\text{P}$ double bond, kinetically stabilized by bulky ligands, has been reported [121]:



One crystallographically authenticated organotin–antimony compound,

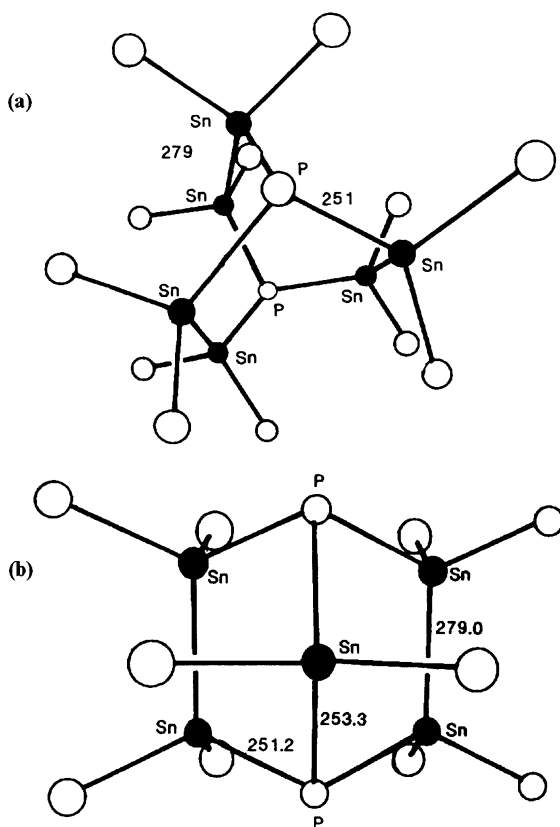


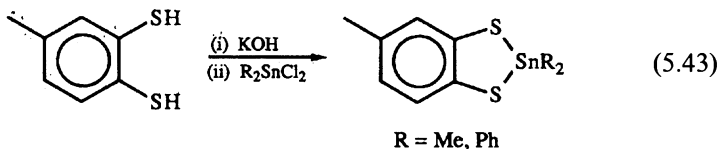
Figure 5.2 The structures of (a) $(\text{Me}_2\text{Sn})_4\text{P}_2$ and (b) $(\text{Me}_2\text{Sn})_3\text{P}_2$ (distances in picometres). (Redrawn by permission from Refs 119 and 120, respectively.)

$(\text{Me}_3\text{Sn})_4\text{Sb}_2$, produced by photolytic coupling of $(\text{Me}_3\text{Sn})_3\text{Sb}$, has an Sn–Sb bond length of 279.7 pm [122].

Further examples of Sn–Group 15 bonds arise in the organotin pseudo-halides $\text{R}_n\text{SnX}_{4-n}$ ($\text{X}=\text{NCS}$, NCO , N_3 etc; $n=2,3$) [22] and the numerous donor–acceptor complexes these and organotin halides form with N, P and As ligands [14].

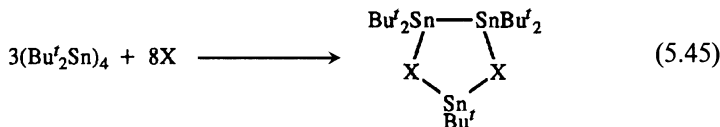
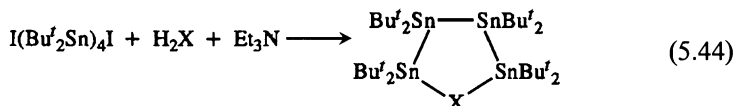
5.3.4 Group 16

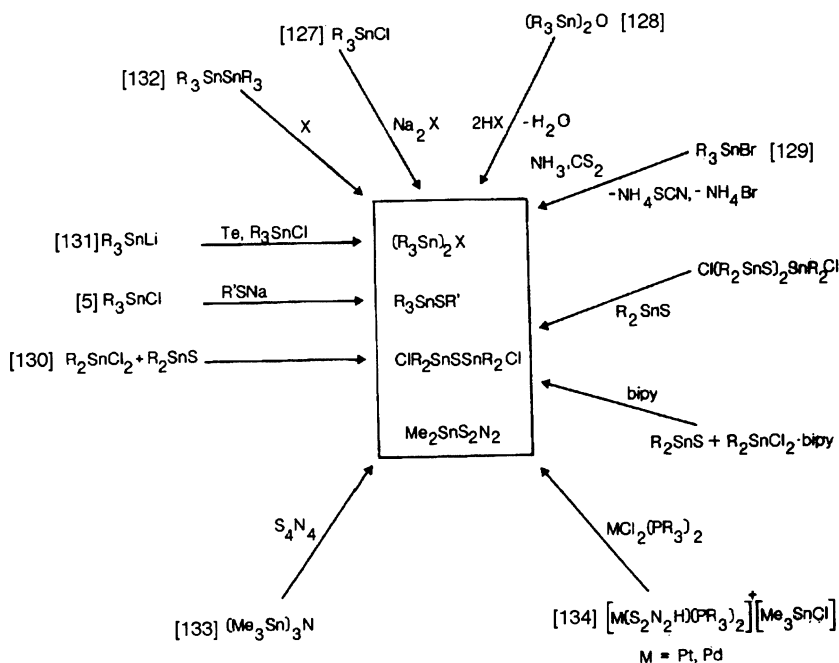
Ease of preparation, high reactivity and diversity of compound type has made Sn–O bonded compounds amongst the most intensively investigated of all organotin systems. Whereas mono- and diorganotin oxides often form amorphous polymers, the corresponding compounds of S, Se and Te tend to form smaller aggregates, and reports of a number of interesting heterocyclic derivatives of these elements with tin have encouraged a resurgence of activity in this area. Simple organotin sulphides and alkyl thiolates have been known for a number of years [123, 124] but a proposal that the biocidal activity of diorganotin compounds arises from binding to enzymatic dithiolates, such as reduced lipoic acid [125], has renewed interest in this area of chemistry also, and several new thiolates have been reported [126].



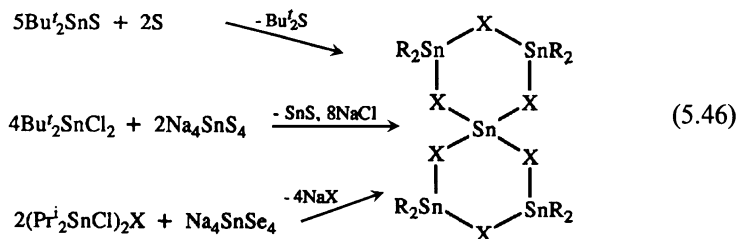
Like many of the corresponding hydroxides, the hydrochalcogenides R_3SnXH ($\text{X}=\text{S}$, Se, Te) readily disproportionate to give bis(triorganotin)chalcogenides. Some preparative methods and reaction chemistry are shown in Scheme 5.9 [127–134]. The Sn–chalcogen bond is less reactive than Sn–O, but Sn–Te bonds are moisture-sensitive.

Several novel tin–chalcogen heterocycles have been synthesized (eqns 5.44–5.46) and their structures determined by crystallographic methods [90, 135, 136].

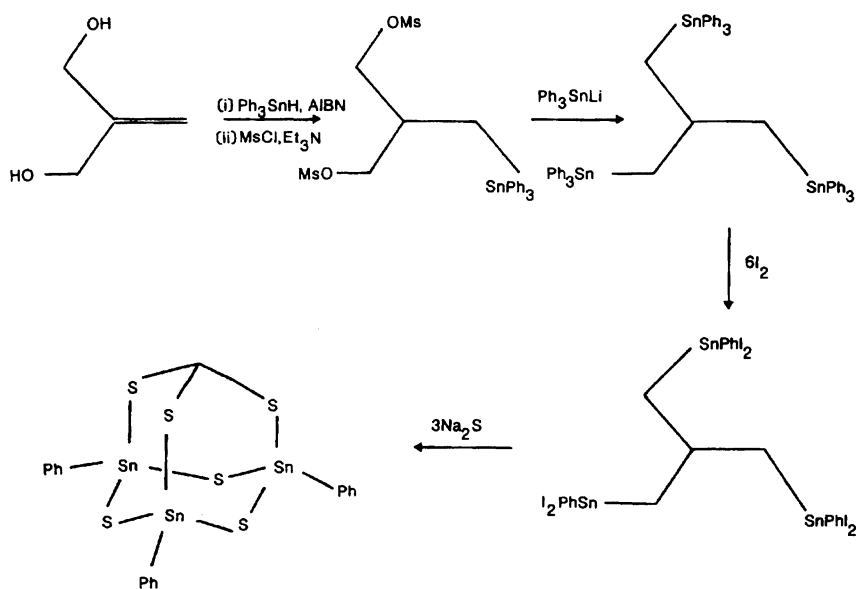




Scheme 5.9 Synthesis and reactions of the organotin-chalcogen bond ($X = S, Se, Te$).



Typical $^1J(^{119}Sn-^{77}Se)$ couplings in these systems are ~ 1500 Hz [136]. Organotin chalcogenides show less tendency to associate via coordinate bonds, thereby expanding the coordination number at tin to five or six, than corresponding compounds containing more electronegative oxygen atoms. For example, $(ClR_2Sn)_2X$ compounds are monomers, except where $X=O$ when they are dimers [137]. However, di- and monoorganotin chalcogenides form ring and cage structures respectively [138–143] (Chapter 2). A polymeric modification of Pr^i_2SnS is also known [144]. 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannadadamantane, whose synthesis is shown in Scheme 5.10, also adopts a cage structure [145]. The apical proton is very labile due to strain at the bridgehead carbon, and this compound is a useful reducing agent in organic synthesis [146].



Scheme 5.10 Synthesis of 1,3-triphenyl-2,4,6-trithia-1,3,5-tristannadamantane.

5.3.5 Groups 3–11, lanthanides and actinides

The formation of bonds between these elements and tin is covered in Chapter 7.

5.4 Structural variations

Arguably the single most important discovery in organotin chemistry was the establishment of $\text{Me}_3\text{SnCl}\cdot\text{py}$ as containing five-coordinated tin. Hulme's X-ray diffraction study in 1963 [147] demonstrated that the maximum coordination number at tin is not confined to four as is normally the case with carbon, and initiated a quarter-century of study which has revealed a structural chemistry as diverse as that of any element of the Periodic Table. Organotin(IV) compounds are now known to contain tin in coordination numbers three through to seven, in varying isomeric forms and lattice arrays. A second legacy of Hulme's work has been the importance of X-ray diffraction studies to the structural tin chemist, and despite the contribution of ^{119}Sn NMR and Mössbauer spectroscopies, no new structural form of tin can be firmly established without crystallographic confirmation. Two compendia of tin crystal structures are currently available for reference [13, 14].

5.4.1 Molecular systems

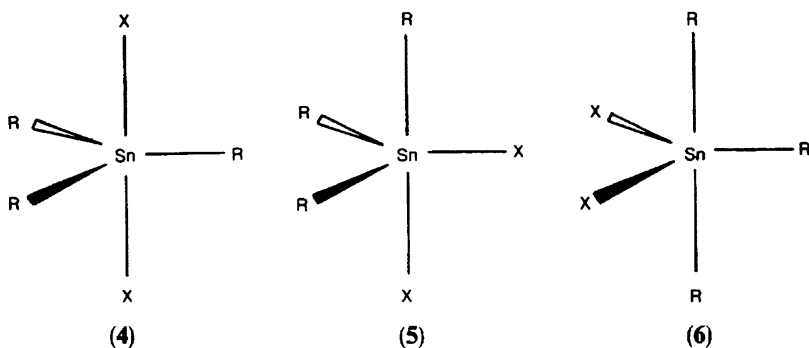
Organotin(IV) compounds are known with coordination numbers (CN) of 3, 4, 5, 6 and 7 at tin, within geometries which are predictable by VSEPR (valence shell electron pair repulsion) methods. However, it should be noted that distortions from regular polyhedra are common and give rise to some of the more debated structural analyses so far reported.

The coordination number adopted by tin in any particular molecule is essentially dictated by two opposing effects: increasing Lewis acidity at the metal, brought about by increasing the number of electronegative substituents on tin, will promote high coordination numbers; conversely, the coordination number at tin will be limited by the steric demands of the ligands, and bulky moieties will favour low coordination numbers. These effects will be evident in the following examples.

Several examples of CN=3, trigonal planar organotin(IV) are known, including the compound containing a $\text{Sn}=\text{C}$ double bond [see structure (1), Chapter 2] stabilized by bulky organic groups. Other trigonal planar organotin(IV) species include the anions R_3Sn^- [71, 218] and examples incorporating other $\text{Sn}=\text{E}$ moieties, e.g. $\text{E}=\text{N}$ [219], transitional metal (Chapter 7). Four-coordinate tin is always of tetrahedral geometry and is typified by a plethora of R_4Sn structures of both symmetric (e.g. $\text{R}=\text{Ph}$ [148], PhCH_2 [149], $\text{C}_6\text{H}_4\text{Me}-2$ [150]) and asymmetric (e.g. $\text{Ph}_3\text{SnCH}_2\text{I}$ [151]) persuasions. When R is replaced by a more electronegative group X , $\text{CN}>4$ usually occurs, although this tendency is checked if X is of relatively low electronegativity (e.g. Br , I vs Cl ; S vs O) or if one or more of the ligands is bulky. The tetrahedral nature of $\text{Me}_3\text{SnS}_2\text{CNMe}_2$ [152], in comparison to $\text{Me}_3\text{SnO}_2\text{CCH}_3$ [153] which is five-coordinated, is a manifestation of the first of these phenomena, while $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{SnCl}$ ($\text{CN}=4$) [154] compared with Me_3SnCl ($\text{CN}=5$) [155] exemplifies the second.

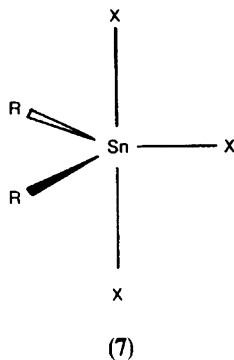
Five-coordinated structures are generally trigonal bipyramidal in shape, and this is commonly the structure adopted by R_3SnX compounds and, to a lesser extent, R_2SnX_2 species. Three isomeric forms are possible for this geometry, of which the *trans* isomer (4) (e.g. $(\text{Bu}_3\text{SnCl}_2)^-(\text{BzPPh}_3)^+$ [156], $\text{Me}_3\text{SnCl}\cdot\text{py}$ [147] or $(3\text{-thienyl})_3\text{SnBr}\cdot\text{Ph}_3\text{PO}$ [157] is more prevalent than the *cis* analogue (5) [e.g. $\text{Ph}_3\text{SnON}(\text{Ph})\text{CO}\cdot\text{Ph}$] [158]). The distribution of structures between these two isomers, and indeed the lack of any *mer*- $[\text{R}_3\text{SnX}_2]$ examples (6), can be rationalized by a qualitative MO analysis [159]. For the *trans*-isomer (Figure 5.3a) the HOMO is a non-bonding MO centred on the two axial ligands X (2a'). This is lowest in energy when the energies of the axial ligands are as low as possible, i.e. X is of high electronegativity. This analysis parallels the 'axially most electronegative' valence bond terminology of Bent [160]. The D_{3h} structure, or distorted versions of it, occur when X (e.g. O , N , halogen) is more electronegative than R , which is usually the case.

For the *cis*- $[\text{R}_3\text{Sn}_2]$ isomer (Figure 5.3b), the effect on the energy of the



non-bonding HOMO, brought about by forming symmetry-adapted axial R and X orbital combinations, is to raise its energy. However, this is minimized, and thus favoured, when the R-AOs are similar in energy to the X-AOs. This geometry is thus more common when X (e.g. S) and R (e.g. C_6H_5) are of similar electronegativity, and bidentate sulphur ligands usually chelate, while for oxygen bridging between axial sites is more usual. For the *mer*-isomer (Figure 5.3c) the non-bonding HOMO is at its highest energy, arising as it does from the symmetry adapted combination of R-AOs, and it is not surprising that no crystallographic examples of this arrangement have been reported. A combination of high electronegativity R (e.g. C_6F_5) and low electronegativity X (e.g. S) will most likely be required to realize this goal. It should also be appreciated that five-coordinated diorganotin compounds always adopt the *cis*- $[\text{R}_2\text{SnX}_3]$ geometry (7), *mer* with respect to the X ligands, which follows from an adaptation of Figure 5.3c and provided X is more electronegative than R which is usual. This is exemplified by the structure of diphenyltin glycylglycinate, $\text{Ph}_2\text{SnGlyGly}$, which adopts this geometry, as shown in Figure 5.4 [161].

The onset of five-coordination (or higher) is readily evident from up-field ^{119}Sn NMR shifts (Chapter 13). Mössbauer QS values are also capable of distinguishing the three isomers (4; $3.00\text{--}4.00\text{ mm s}^{-1}$), (5; $1.70\text{--}2.40\text{ mm s}^{-1}$) and (6; $3.50\text{--}4.10\text{ mm s}^{-1}$), but tetrahedral R_3SnX species ($1.00\text{--}2.40\text{ mm s}^{-1}$)



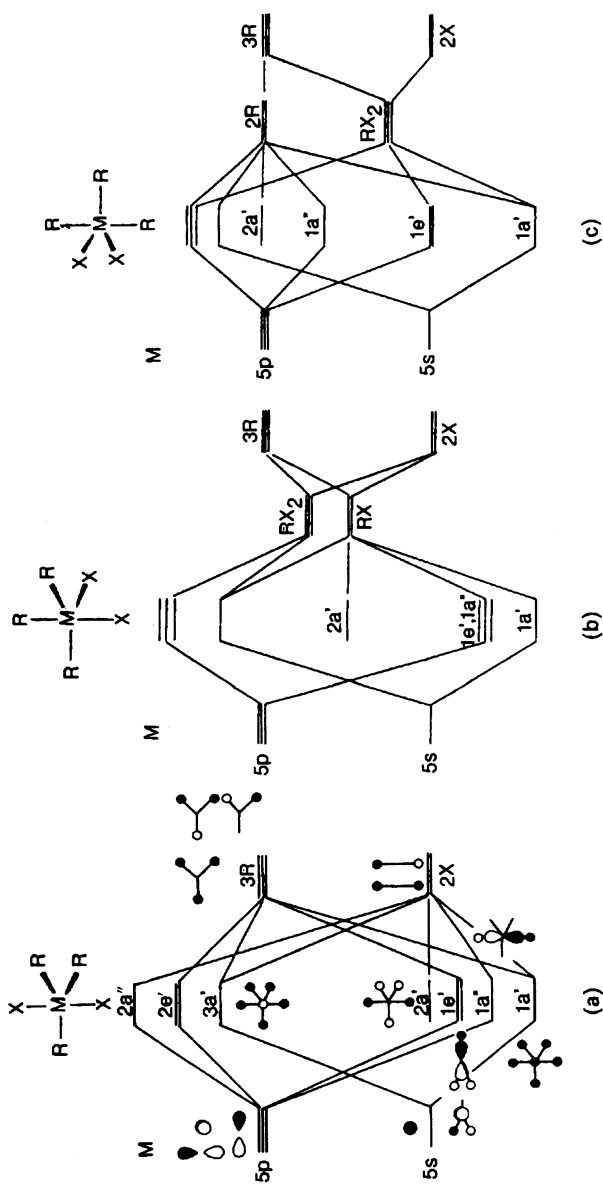


Figure 5.3 Qualitative molecular orbital energy level diagrams for (a) *trans*-[X₂SnR₃], (b) *cis*-[X₂SnR₃] and (c) *mer*-[R₃SnX₂] structures. Although the symmetry labels for MOs are correct only for (a), they have been retained throughout to allow comparison of orbital energies between the three isomers.

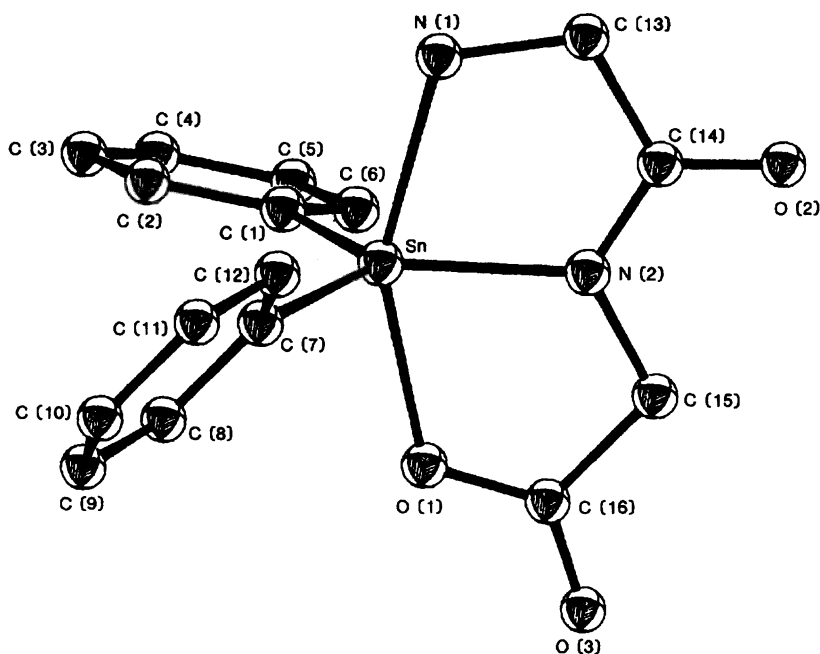
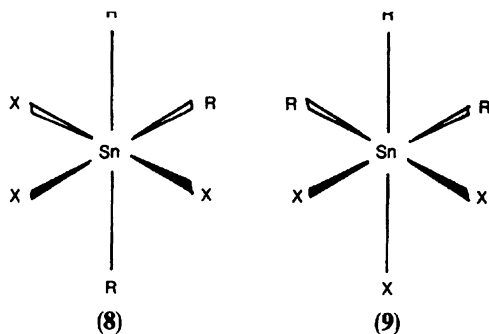


Figure 5.4 The structure of $\text{Ph}_3\text{SnGlyGly}$. (Redrawn by permission from Ref. 161.)

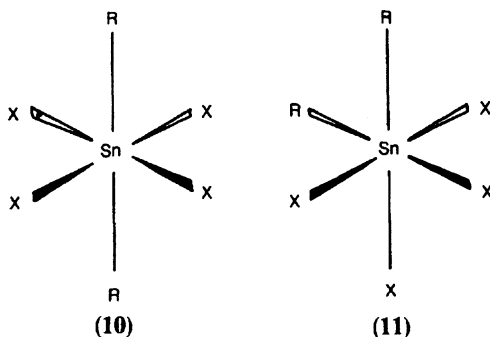
can be confused with the *cis* configuration, particularly when the QS of the tetrahedral species is enhanced by deviations from ideal geometry (see also Chapter 14) [5].

Six-coordinate systems are common for the highly Lewis-acidic R_2SnX_2 , RSnX_3 classes, but rare for tetra- and triorganotin. Bis[3-(2-pyridyl)-2-thienyl-*C,N*]diphenyltin(IV) [162] is unique in being the only six-coordinated tetraorganotin compound, although a five-coordinated stannatrane $\text{MeSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ has been reported [163], as have unsubstantiated claims for the adduct $\text{Me}_3\text{SnCF}_3 \cdot \text{hmpa}$ [164]. R_3SnX species with $\text{CN}=6$ are equally rare, but one example each of both *mer*-(8) and *fac*-(9) isomers is



known. The latter is formed using the tridentate tris(pyrazolyl)borate ligand, and its complex with $\text{Me}_3\text{Sn-}$ is shown in Chapter 2, structure (52) [165]. The *mer* isomer is less clear cut and occurs in the coordination polymer $\text{Ph}_3\text{SnO}_2\text{CCH}_3$, but the sixth bond is very weak (Sn-O , 320.6 pm) [166]. Again, Mössbauer QS values are predicted to be quite different for the two forms [(8), $\text{QS} \sim 3.50 \text{ mm s}^{-1}$; (9), $\text{QS} \sim 0 \text{ mm s}^{-1}$]. Data for $\text{Ph}_3\text{SnO}_2\text{CCH}_3$ ($\text{QS} = 3.36 \text{ mm s}^{-1}$) are consistent with the *mer*-isomer value, but five-coordinated *trans*- O_2SnR_3 systems give too similar a QS value for this experiment conclusively to authenticate $\text{CN} = 6$. Both Mössbauer and ^{119}Sn NMR data are, unfortunately, still outstanding for the six-coordinated *fac*- compound.

Six is the common coordination number for diorganotin systems. Both *trans*-(10) and *cis*-(11) isomers are known, the former being markedly more common. Adducts of $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2$ with 4,4'- $\text{Me}_2\text{bipy}(2,2')$ occur in both

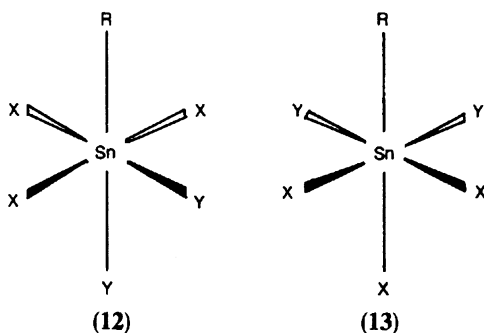


cis and *trans* forms, which isomerize in solution [167]. This is the only confirmed example in which both isomers of the same compound have been isolated, so clearly a fine balance of as yet undetermined factors has fortuitously been achieved in this instance. $\text{Ph}_2\text{Sn}[\text{S}_2\text{CNET}_2]_2$ exemplifies the less common *cis* isomer [168] which, empirically, seems to be more favoured by the presence of two bidentate, rather than four monodentate, ligands. This latter compound is, however, distorted, and this is a common feature of this geometry.

The structure of $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ [169] highlights two other structural features common to distorted $[\text{R}_2\text{SnX}_4]$ geometries. First, the C-Sn-C bond angle is a function of the strength of the fifth and sixth bonds to tin, arising from the chelating ligands, and weak, anisobidentate chelation results in only slight opening of the C-Sn-C skeleton (137.3°) from 109° towards 180° . When chelation is symmetrical or isobidentate, a linear C-Sn-C arrangement accrues, e.g. $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OPr}')_2]_2$ [170]. Second, bond lengths within the ligand should reflect its coordinating strength to tin. In the dithiocarbamate, anisobidentate chelation results in C-S and C=S which have clearly distinguishable bond lengths. Isobidentate chelation, as in the thiophosphate, induces a totally delocalized S-P-S system, with S-P bonds of equal length. These

ligand bond length patterns therefore provide important ancillary evidence concerning the validity or otherwise of weak, coordinate tin–donor bonds. (A discussion of distorted octahedral complexes in terms of a skew-trapezoid bipyramid can be found in Ref. 171.)

Monoorganotin compounds are also strongly Lewis-acidic, and readily form six-coordinated structures. Monoorganotin trihalide complexes with O, N and S donor ligands of stoichiometry $\text{RSnX}_3 \cdot 2\text{L}$ are common examples of this effect. Two isomeric forms, *mer* (**12**) and *fac* (**13**), are possible, and can be distinguished by Mössbauer QS values by comparison with the predicted



values based upon a point charge model. The BuSnCl_3 adducts with either $\text{Ni}(\text{salphen})$ or $\text{Ni}(\text{salmphen})$ can produce either isomer depending on crystallization solvent, but have not yet been characterized crystallographically [172].

Seven-coordinated organotin compounds have been less extensively studied, and considerable scope for further study exists in this area. Both mono- and diorganotin systems can achieve this coordination number, and universally adopt a pentagonal bipyramidal geometry. An example involving a pentadentate ligand, $\text{Ph}_2\text{Sn}(\text{dapa})$ [173], is shown in Figure 5.5, but these are less common than monoorganotins bound to three bidentate ligands, e.g. $\text{MeSn}(\text{NO}_3)_3$ [174], or adducts incorporating ligands of lower denticity, e.g. $\text{Me}_2\text{Sn}(\text{NCS})_2 \cdot \text{terpy}$ [175] or $\text{Ph}_2\text{Sn}(\text{NO}_3)_2 \cdot \text{Ph}_3\text{PO}$ [176]. All compounds of this coordination number are characterized by extremely high-field (c. -450 to -700 ppm) ^{119}Sn chemical shifts in their NMR spectra [177].

5.4.2 Rings, ladders and chains

The examples chosen to depict organotin(IV) coordination spheres in the preceding section centred exclusively, with the exception of triphenyltin acetate, on discrete, molecular systems. It is, however, one of the fascinating aspects of this area of chemistry that molecules will associate through their ligands to produce clusters of increasing complexity, from dimeric units to three-dimensional networks.

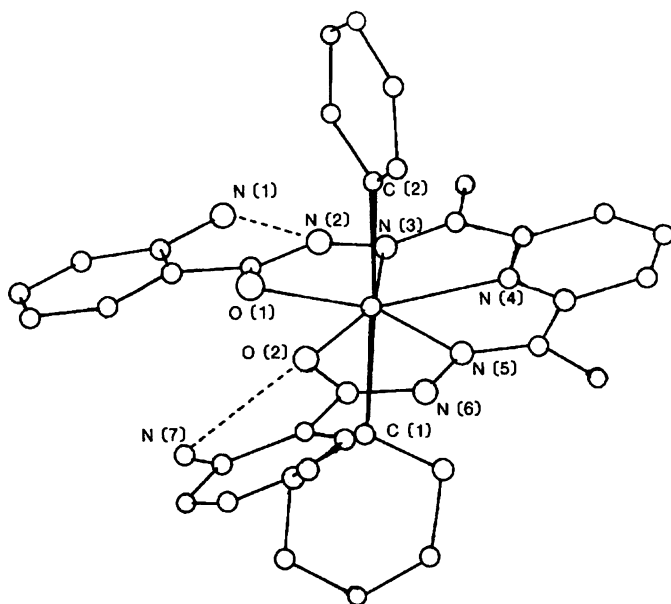


Figure 5.5 The structure of $\text{Ph}_2\text{Sn}(\text{dapa})$. (Redrawn by permission from Ref. 173.)

Molecular association in one dimension to form linear coordination polymers is one of the more common lattice structures in organotin chemistry. Me_3SnX { $\text{X}=\text{Cl}$ (Figure 5.6a) [115], OMe [178], NCS [179], N_3 [180]} are typical, and all are based upon a *trans*- $[\text{X}_2\text{SnR}_3]$ repeat geometric unit. Uniquely, and without obvious rationale, Me_3SnOH adopts a structure which eclipses CH_3 -groups, and places all the oxygen atoms on the same side of the polymer spine (Figure 5.6b) [181]. This structure is made more surprising by the fact that Ph_3SnOH [182] crystallizes in the conventional array of Figure 5.6a.

Diorganotin dihalides (Me_2SnCl_2 [183], Et_2SnX_2 ; $\text{X}=\text{Cl}, \text{Br}, \text{I}$ [184]) form similar one-dimensional chains, now with double halide bridges. Figure 5.7 shows the arrangement for Me_2SnCl_2 . It is clear from this pictorial representation that the octahedral $[\text{Me}_2\text{SnCl}_4]$ unit is not regular and the non-linear C-Sn-C unit arises in this case from the weak, intermolecular $\text{Cl}\cdots\text{Sn}$ bridging bonds in a manner analogous to that described for molecular, chelated species. These deviations in molecular geometry at tin for varying strengths of intermolecular bonding are nicely visualized as frozen pictures of points along a reaction pathway for a nucleophilic displacement reaction. $\text{S}_{\text{N}}2$ substitution with inversion at a tetrahedral centre is thus depicted by polymeric *trans*- $[\text{R}_3\text{SnX}_2]$ geometries, whose structures map the reaction profile for this reaction (Figures 5.8). As the intermolecular $\text{Y}\cdots\text{Sn}$ bond becomes stronger, so the intramolecular Sn-X bond weakens and the

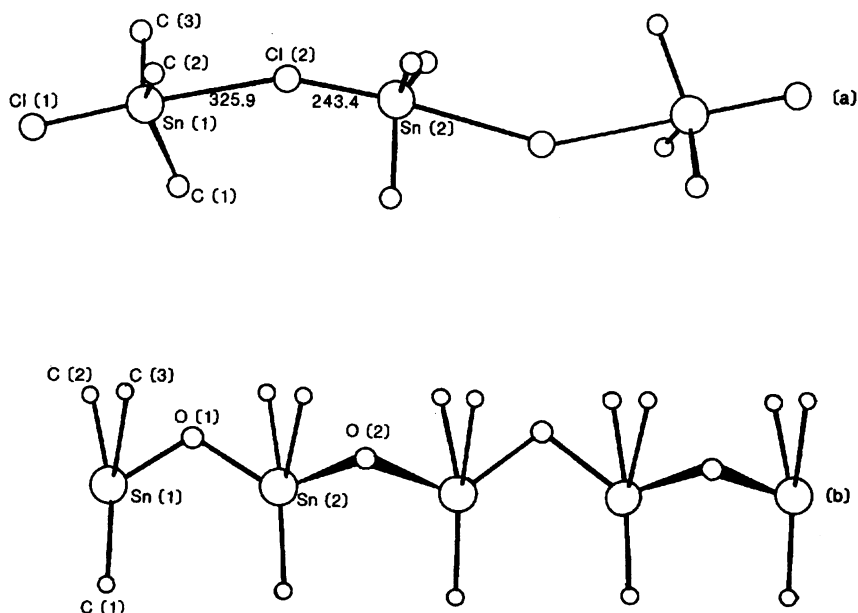


Figure 5.6 The structure of (a) Me_3SnCl and (b) a provisional analysis of the crystallographic data for Me_3SnOH (distances in picometres). [(b) Redrawn by permission from Ref. 181.]

C–Sn–X bond angle closes towards 90° . A regular $[\text{R}_3\text{SnX}_2]$ trigonal bipyramid with equal Sn–X, Sn–Y bonds corresponds to the $\text{S}_{\text{N}}2$ transition state [185].

The manner in which the coordination polymer propagates through space is determined by the steric demands of both the hydrocarbon and ligand

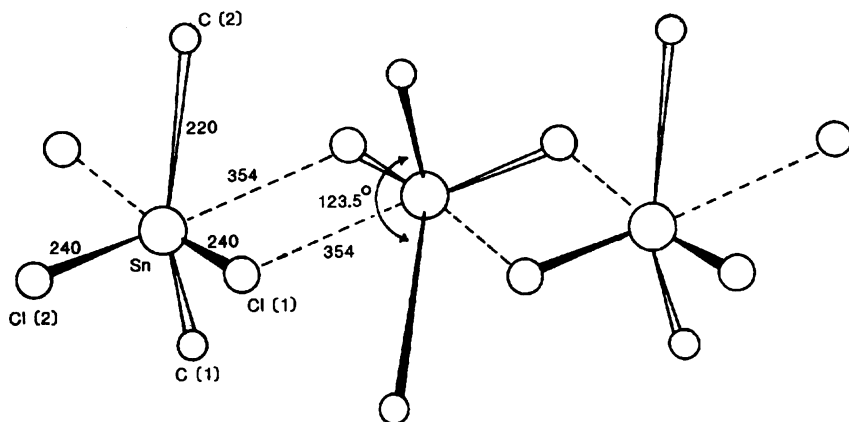


Figure 5.7 Part of the Me_3SnCl_2 coordination polymer (distances in picometres). (Redrawn by permission from Ref. 183.)

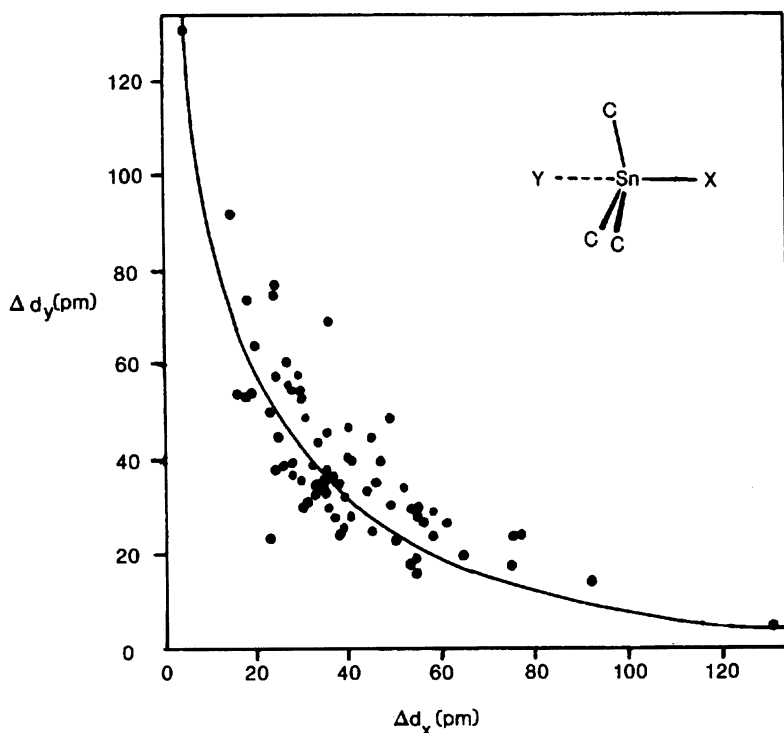


Figure 5.8 Correlation diagram for intra- and intermolecular bonds in polymeric *trans*-[R₃SnXY] systems indicating the analogy with the S_N2 reaction profile. $\Delta d_Y = d(\text{Sn-Y})_{\text{obs}} - d(\text{Sn-Y})_{\text{single}}$; Δd_X is defined analogously. (Redrawn by permission from Ref. 185.)

residues. The polymer spines of Ph₃SnO₂CR (R = H, Me) are shown in Figure 5.9. Bending of the acetate chain to minimize steric clashes between CH₃ and C₆H₅ is visually apparent [186]. As the bulk of substituents on tin or the acid increases, polymer bending becomes accompanied by a weakening of the intermolecular bond, e.g. (C₆H₁₁)₃SnO₂CMe [187], until finally only tetrahedral monomers are possible, e.g. Ph₃SnO₂CCMe₃ [188].

Coordination polymers which have CN > 4 at tin can be distinguished from discrete molecules with the same metal coordination number by comparison of solution and solid state spectra. Intramolecular coordination is retained in solution, whereas intermolecular bonds are concentration dependent with complete polymer fragmentation accompanied by lowering of the tin coordination occurring in dilute solutions, and both IR and NMR methods can be used to investigate such phenomena (see Chapter 13).

Lattice association into two dimensions begins with the formation of cyclic oligomers, which then continue to link together into small sheets or 'ladder' arrays. Of the cyclic oligomers, dimers and trimers are well characterized, and

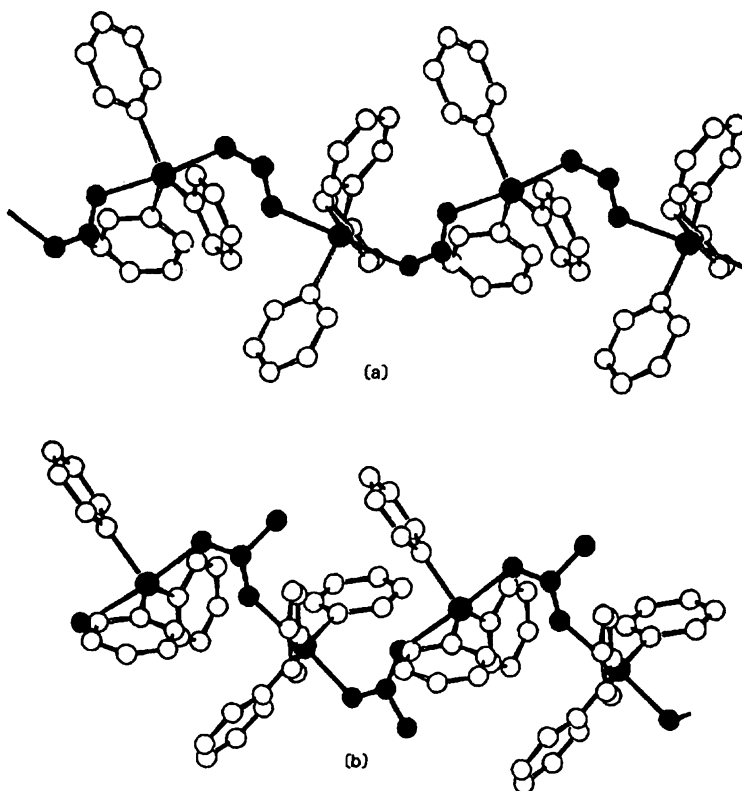
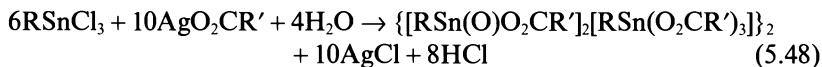
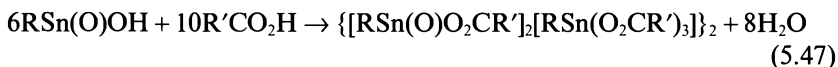


Figure 5.9 Polymer propagation in $\text{Ph}_3\text{SnO}_2\text{CR}$, (a) $\text{R}=\text{H}$, (b) $\text{R}=\text{CH}_3$. (Data from Ref. 186.)

exemplified by the auto-dimerization of organotin alkoxides. The enhanced coordination number at tin in the dimer is reflected in changes in ^{119}Sn NMR shifts [189, 190]. Steric bulk on the OR' ($\text{R}'=\text{Pr}^i$, Bu^s , Bu') ligand inhibits dimer formation, and this effect similarly influences the degree of nuclearity of diorganotin chalcogenide oligomers, viz $(\text{Me}_2\text{SnX})_3$ vs $(\text{Bu}'_2\text{SnX})_2$ ($\text{X}=\text{S}$, Se) [139–141, 191]. The largest ring system known that is formed in cyclic coordination is hexameric $[\text{Ph}_3\text{SnO}_2\text{P}(\text{OPh})_2]_6$ [192] (see Figure 2.6).

Ladder structures, which are essentially a fusion in one direction of small rings, are particularly a feature of tin–oxygen compounds (probably due to the widespread occurrence of $[\text{Sn}_2\text{O}_2]$ ring systems) and several examples have been published. Hydrolysis of Me_2SnCl_2 yields $[\text{HNEt}_3][(\text{Me}_2\text{SnCl})_5\text{O}_3]$ [193] and is clearly part of Scheme 5.4, although this product cannot be obtained by rational synthesis. Reproducible syntheses of ladder monoorganotin carboxylates have been devised by two methods [55, 194]:



The structure of $[\text{Bu}^n\text{Sn}(\text{O})\text{O}_2\text{CPh}]_2[\text{Bu}^n\text{Sn}(\text{O}_2\text{CPh})_3]$ is illustrated in Figure 5.10 [55]. Longer oligomeric [195] and also polymeric [196] ladder structures have been characterized for 1,3,2-dioxastannolanes and related systems.

5.4.3 Layer compounds

When intermolecular association takes place in two dimensions, layer structures result. Examples of this structural type are relatively rare, particularly in comparison with one-dimensional chain compounds, probably since increasing association reduces solubility and inhibits the growing of crystals. Most of the available examples occur with diorganotin halides or pseudo-halides, e.g. Me_2SnF_2 [197], $\text{Me}_2\text{Sn}(\text{CN})_2$ [198], $\text{Me}_2\text{Sn}[\text{N}(\text{CN})_2]_2$ [199]. Figure 5.11 shows a further example, $\text{Me}_2\text{Sn}(\text{SO}_3\text{F})_2$ [200].

5.4.4 Cages and networks

Monoorganotins naturally incorporate three ligands, and are thus potentially able to form three-dimensional arrays. Where small cages, rather than extended networks, are formed, solubility is likely to be more favourable, and

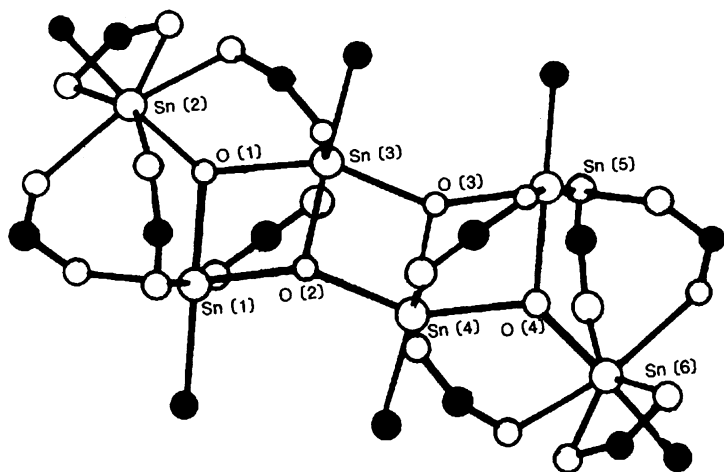


Figure 5.10 The structure of $[\text{Bu}^n\text{Sn}(\text{O})\text{O}_2\text{CPh}]_2[\text{Bu}^n\text{Sn}(\text{O}_2\text{CPh})_3]$. Phenyl groups and all but the α -carbon atoms of the butyl chains have been omitted for clarity. Carbon atoms are shown as \bullet . (Redrawn by permission from Ref. 55.)

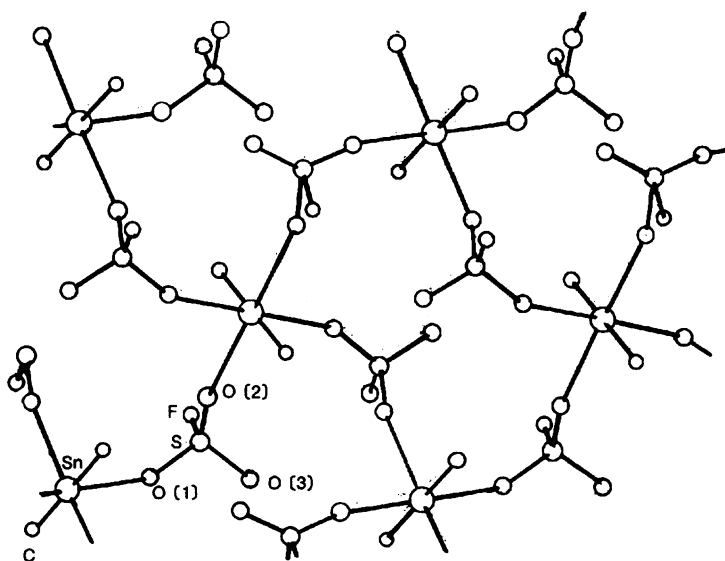
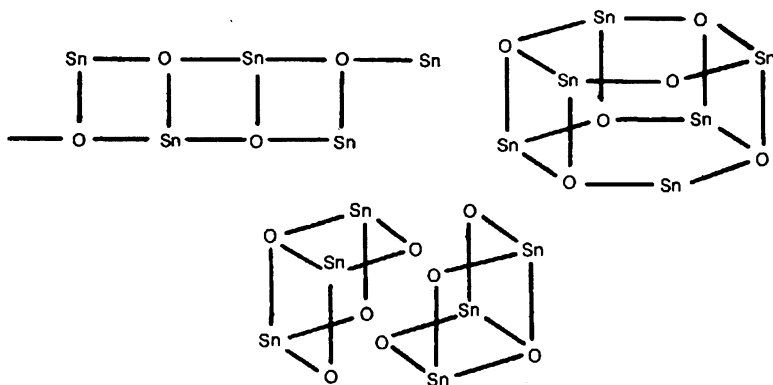
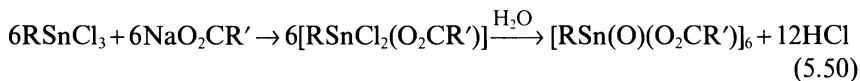
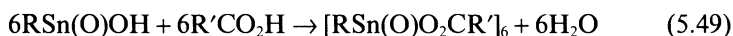


Figure 5.11 The layer structure of $\text{Me}_3\text{Sn}(\text{SO}_3\text{F})_2$. (Redrawn by permission from Ref. 200.)

among the organotin derivatives of Groups 15 and 16 trigonal bipyramidal, cubic and adamantane cages have already been described. Of these, only the latter has been established crystallographically. To add to this range, a rather more exotic class of monoorganotin-oxygen compounds has appeared, which can be related to the ladder stannoxane of Figure 5.10. Scheme 5.11 shows how the ladder can be considered as an 'open drum', and by hydrolysis converted to a 'drum' structure. Synthesis of the drum, as with the ladder, originates with either a stannous acid or organotin trihalide [55, 194, 201].



Scheme 5.11 The relationship between ladder, drum and oxo-capped cage structures.



Two representations of a typical 'drum' structure, $[\text{Bu}''\text{Sn(O)O}_2\text{CC}_5\text{H}_9]_6$, are shown in Figure 5.12. If bulkier ligands are present, a cubic tetrameric analogue of the drum of identical empirical formula and exemplified by $[\text{Bu}''\text{Sn(O)O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$ [202] (Figure 2.7) results. An oxo-capped trisnnoxane arises from what is formally hydrolysis of the drum arrangement (Scheme 5.11), an example of which is $[\text{Bu}''\text{Sn(OH)O}_2\text{PPh}_2]_3\text{O}]^{+}[\text{Ph}_2\text{PO}_2]^{-}$ [203] (Figure 2.8). All of these structures, including the ladder, derive from the SnOSnO moiety, so cages with even numbers of tin atoms appear to predominate over odd-tin arrays which are subsequently derived from them.

Crystalline network structures are relatively rare, but occur when an organotin is bonded to a polyfunctional ligand. $(\text{Me}_3\text{Sn})_3[\text{Co}(\text{CN})_6]$ is an example [204].

5.4.5 The solution state

Two topics are important when considering structure in solution. Firstly, what species are present, are there equilibria operating and are these solvent-dependent? Secondly, to what extent can data from the solid state – X-ray diffraction, Mössbauer spectroscopy – be correlated with species in solution? Studies relating to the first of these questions are remarkably limited, and even for aqueous media and the attendant environmental implications, the equilibria of Tobias (Figure 5.13) for methyltin systems remain the most significant contribution [205]. Two solvated cations, $[\text{Bu}_3\text{Sn}(\text{H}_2\text{O})_2]^{+}$ [206] and $[\text{C}_y_3\text{Sn}(\text{NCMe})_2]^{+}$ [207], both of which exhibit trigonal bipyramidal geometry at tin, have now been established crystallographically. The former is of clear environmental relevance, while the latter type of structure has been impli-

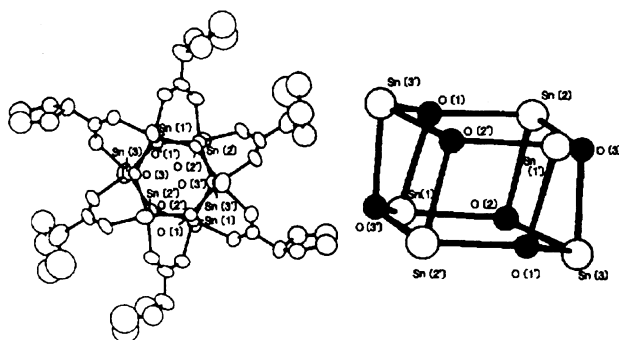


Figure 5.12 Two representations of the drum architecture of $[\text{Bu}''\text{Sn(O)O}_2\text{CC}_5\text{H}_9]_6$. Only the α -carbon atoms are included for clarity. (Redrawn by permission from Ref. 194.)

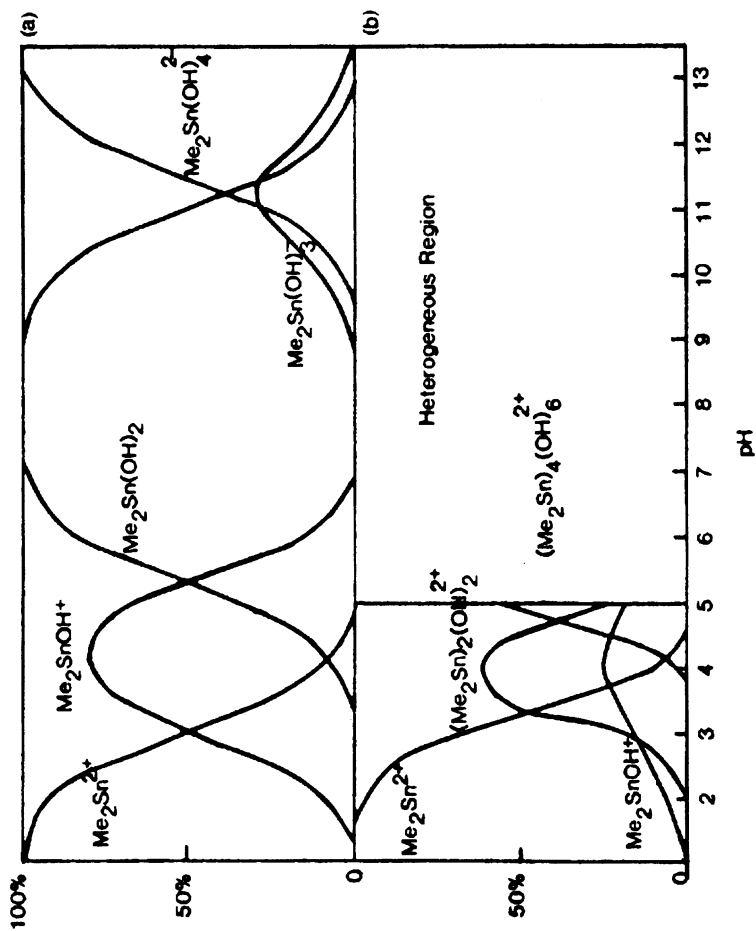


Figure 5.13 Species distribution diagrams for aqueous solutions of dimethyltin at (a) 10^{-5} M and (b) 10^{-3} M. (Redrawn from Ref. 205.)

cated in the racemization of optically active triorganotin halides [208]. Furthermore, products which are isolated in the solid state may be the least soluble rather than the thermodynamically favoured reaction product, and other species may predominate in solution. Equilibrium constants for the formation of adducts of di- and triorganotin halides have been measured by ^{31}P NMR and calorimetry, and suggest that in both cases 1:1 products are favoured, and that the dominance of $\text{R}_2\text{SnCl}_2 \cdot \text{L}_2$ species in the solid state merely reflects their lower solubility [209, 210].

Structurally, solid state geometries and coordination numbers will generally hold for the solution state only if intermolecular coordination is absent. However, structural dynamics must also be considered in solution, and many fluxional organotin compounds are known. Of these, derivatives of cyclopentadiene and related carbocycles are the most celebrated, and have been widely studied by NMR methods [211]. Two-dimensional NMR methods have also been used to investigate structural equilibria [212] and no doubt more use will be made of this technique in coming years.

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6 Organometallic compounds of bivalent tin

PAUL D. LICKISS

6.1 Introduction and review articles

The last 10 years have seen steady growth in the number of investigations into the chemistry of organometallic R_2Sn species. Much of this work has concentrated on the chemistry of relatively stable stannylenes and stannocenes and the preparation of new, even more stable compounds. The potential for bivalent organometallic tin species in organic synthesis has also been studied. This chapter includes a description of the work covered in the first edition but concentrates on work published since 1988.

Early work on the nature of stannylenes has been reviewed by Neumann [1] and an article by Connolly and Hoff [2] in 1981 gives a good review of the work done up to about 1979. More recent work on stannylenes has also been reviewed by Neumann [3], Mackay [4] and Davies [5]. Transition metal complexes of silylenes, germylenes, and plumbylenes as well as stannylenes have been reviewed [6,7] as has the chemistry of stannocenes and other Group 14 π -complexes [8].

6.2 σ -Bonded compounds

6.2.1 *Synthesis*

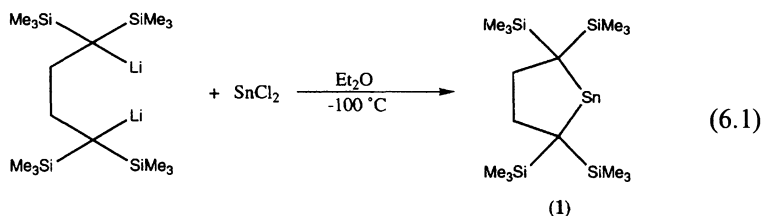
Simple dialkyl- and diaryltins, R_2Sn ($R=Me, Ph$, etc.) are thought to be reactive intermediates in many reactions, but in the absence of trapping reagents, cyclic, linear or branched oligomers are formed (a recent review of such tin(IV) compounds has appeared [9]). An example of such a reaction is the reaction of 9-phenanthrylmagnesium bromide with $SnCl_2$ [10] which yields a mixture of cyclic, open-chain and polymeric stannanes rather than di(9-phenanthryl)tin as earlier work had suggested [11]. However, simple R_2Sn species may be trapped either at low temperature in a matrix, or chemically. For example, dimethylstannylene, Me_2Sn , is formed when 2,2,3,3,5,5,6,6-octamethyl-1,4-ditellura-2,3,5,6-tetrastannacyclohexane is photolysed. This can then be trapped with CH_3I to give Me_3SnI [12]. Treatment of $SnCl_2$ with $LiCHCl_2$ at $-78^\circ C$ in THF solution gives rise to a product formulated as $(CHCl_2)_2Sn \cdot xTHF$, but attempts to remove the non-coordinated THF result in the formation of oligomers, making characterization of the compound difficult [13]. Evidence for the formation of $(CF_3)_2Sn$

and CF_3SnI in the equilibration reaction between SnI_2 and $(\text{CF}_3)_2\text{Cd}$ has been obtained by ^{19}F NMR and Mössbauer spectroscopy [14].

Neumann *et al.* [15, 16] have developed methods for preparing a variety of R_2Sn species in solution at 20°C from the thermal decomposition of 7-stannanorbornenes or at -30°C by reduction of R_2SnCl_2 by 2Li-anthracene ($\text{R} = \text{CH}_3, \text{CD}_3, \text{Et}$ or Bu'). The thermolysis of cyclohexastannanes and subsequent trapping in an argon matrix at 5 K is also a good clean source of monomeric Me_2Sn and $(\text{CD}_3)_2\text{Sn}$ which has enabled a detailed IR spectroscopic study to be carried out [17].

Although transient alkyltin(II) species were thought to be present in many reaction systems and evidence for them could be gained by trapping experiments, the synthesis of a stable dialkyltin(II) compound remained a challenge for many years. The solution to this problem has been the use of sterically bulky substituents on the tin to prevent oligomerization. Thus, Lappert *et al.* used the sterically demanding bis(trimethylsilyl)methyl ligand to prepare bis[bis(trimethylsilyl)methyl]tin(II) which is kinetically stable with respect to oligomerization [18, 19]. (For a discussion of its monomer, dimer equilibria, see section 6.2.2) Several synthetic routes are available: reaction of SnCl_2 , $(\text{Me}_3\text{C}_5)_2\text{Sn}$ or $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ with $(\text{Me}_3\text{Si})_2\text{CHLi}$, or the reduction of the corresponding dialkyltin(IV) dichloride with Li_2cot [18–21].

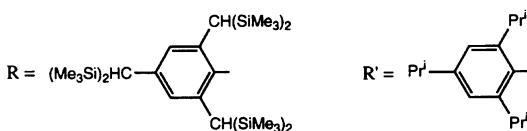
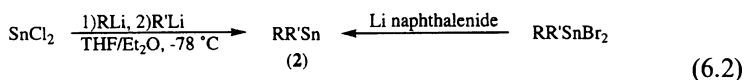
The first dialkylstannylene (1), that is a two coordinate monomer in the solid state is structurally similar to the now well known $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ and it can be prepared as dark red, moisture-sensitive crystals according to eqn 6.1. The decrease in flexibility, and the cyclic nature of the stannylene are probably both factors that favour the monomeric structure over the dimeric nature of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ [22]. A structurally related cyclic stannaindene $[o-(\text{Me}_3\text{SiCH})_2\text{C}_6\text{H}_4]\text{Sn}$ may be obtained from a dilithium reagent and either a tin(IV) or (in better yield) a tin(II) precursor. It is, however, tetrameric in the solid state with an Sn_4 ring with the four tin atoms in a distorted tetrahedral arrangement, but in the gas phase the compound is thought to be monomeric [23].



In recent years the use of bulky aryl ligands has become more widely studied as substituents capable of preventing oligomerization of divalent tin species. If the reaction of 2,4,6- $\text{Pr}_3\text{C}_6\text{H}_2\text{Li}$ with SnCl_2 in Et_2O is carried out at -80°C and the reaction mixture is kept below -30°C the product is the monomeric stannylene $(2,4,6\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{Sn}$. If the solution is allowed to

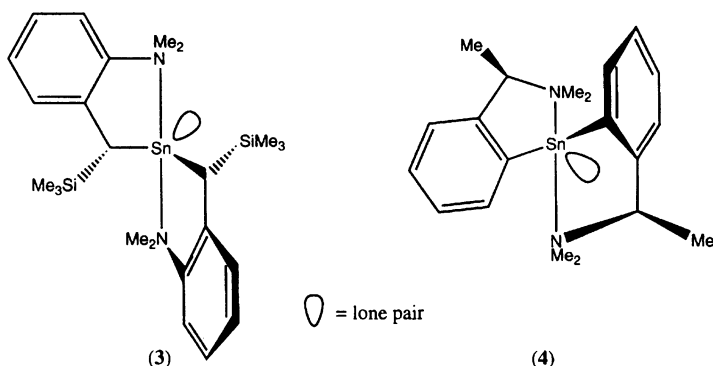
warm to room temperature the cyclic trimer $[(2,4,6\text{-Pr}_3^i\text{C}_6\text{H}_2)_2\text{Sn}]_3$ is formed instead [24, 25]. Photolysis of the cyclotrimer in the presence of various trapping agents gives products derived from the stannylene dimer [26]. Stable diaryltin(II) compounds are, however, formed as products in the reactions of SnCl_2 with aryllithium reagents bearing more bulky *ortho*- and *para*-alkyl substituents [27]. The most studied of these stannylenes is $[2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ which is formed in 45% yield as an air-sensitive yellow solid [28]. Although it has not been found possible to isolate the highly hindered diaryl stannylene $(2,4,6\text{-Bu}_3^i\text{C}_6\text{H}_2)_2\text{Sn}$ from the reaction between SnCl_2 and $2,4,6\text{-Bu}_3^i\text{C}_6\text{H}_2\text{MgBr}$, it can be isolated in 64% yield as dark red crystals from the reaction between the amide $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ and $2,4,6\text{-Bu}_3^i\text{C}_6\text{H}_2\text{Li}$. The stannylene is, however unstable in solution, one of the aryl groups isomerizing, as described in section 6.2.2 [29]. The reaction between ArMgBr ($\text{Ar} = 2\text{-Bu}^i\text{-4,5,6-Me}_3\text{C}_6\text{H}$) with SnCl_2 gives a red solution containing a monomer dimer equilibrium of the expected stannylene. On crystallizing from *n*-hexane, only the dimer is isolated as black crystals in 30% yield [30].

The kinetically stabilized stannylene (2) may be prepared either by sequential reaction of lithium reagents with SnCl_2 or, better, by reduction of the diaryldibromostannane (eqn 6.2). It is deep purple in hexane solution ($\lambda_{\text{max}} = 561 \text{ nm}$) and has a ^{119}Sn NMR chemical shift of 2208 ppm, in the region expected for a divalent organometallic tin [31, 32].



Reaction between SnCl_2 or Cp_2Sn with $o\text{-LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ gives monomeric, four-coordinate ($o\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2$) $_2\text{Sn}$ [33]. The reaction of SnCl_2 with racemic $\text{Li}[\text{CH}(\text{SiMe}_3)(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)]$ proceeds diastereoselectively to give what, on steric grounds, is thought to be the four-coordinate isomer (3). Similarly the chiral (4) can be prepared from SnCl_2 and enantiomerically pure $\text{Li}[\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-(R)-}2]$ [34, 35]. The chemistry of compounds with intramolecular coordination to bivalent tin has been reviewed in detail [36].

Treatment of SnCl_2 with $(\text{PPh}_2)_2\text{CHLi}$ leads to formation of a three-coordinate Sn(II) species, $[(\text{PPh}_2)_2\text{CH}]_2\text{Sn}$, in which one ligand bonds through carbon and the other acts as a chelating diphosphinomethanide. The methyl analogue, $[(\text{Me}_2\text{P})_2\text{CH}]_2\text{Sn}$, has four-coordinate tin with two chelating



diphosphinomethanide ligands and no tin–carbon bonds. ^{31}P NMR spectroscopy suggests that at 50°C the structure of $[(\text{PPh}_2)_2\text{CH}]_2\text{Sn}$ is similar to that of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$, i.e. with the tin bonded to the two central carbon atoms of the ligands [37–39].

6.2.2 Structure

The various calculations on the geometry and energies of Group 14 MH_2 species and the importance of relativistic effects have been discussed in detail [40]. Relativistic configuration interaction calculations on SnH_2 give a singlet–triplet energy separation of about 105 kJ mol^{-1} and a geometry comprising an Sn–H distance of 1.785 \AA and an H–Sn–H angle of 91.1° for the lowest lying electronic state [41]. Quasi-relativistic *ab initio* model potential calculations for SnH_2 give values of 1.768 \AA , 92.32° and 1833 cm^{-1} for the Sn–H length, H–Sn–H angle and symmetric stretching frequency, respectively [42]. The singlet–triplet splitting $^1A_1\text{--}^3B_1$ for SnH_2 using local spin density [43] or SCF + CI calculations [44] gives a value of about 98 kJ mol^{-1} . Similar calculations also show that for the Sn_2H_4 potential surface a $\mu\text{-H}$ -bridged structure has the minimum energy, the *trans*-bent structure being the least stable [44].

Matrix isolation techniques have enabled the IR spectra of both Me_2Sn and $(\text{CD}_3)_2\text{Sn}$ to be recorded at 5 K . The trapped stannylenes have C_{2v} symmetry and Sn–C stretching frequencies in Me_2Sn of 518 and 504 cm^{-1} [17]. *Ab initio* SCF calculations using a pseudopotential method give an Sn–C bond length of 2.203 \AA , a C–Sn–C bond angle of 95.3° and a dipole moment of 0.43 D for Me_2Sn with a singlet ground state [17]. Dewar *et al.* [45] have also calculated parameters for Me_2Sn as a singlet ground state, ΔH_f of 1.25 kJ mol^{-1} , dipole moment of 2.94 D , ionization potential of 9.63 eV , Sn–C bond length of 2.03 \AA and C–Sn–C bond angle of 99.1° . No explanation for the significant differences between the results of the two calculations

for bond length and angle and dipole moment appears to have been given. The structure of the brick-red solid $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ has been determined by X-ray crystallography and is a non-planar centrosymmetric dimer with an Sn–Sn distance of 2.768(1) Å [18, 19, 46]. In cyclohexane or benzene solution it is, however, monomeric at low concentrations [18], although at higher concentrations in $\text{C}_6\text{D}_5\text{CD}_3$ ^{13}C NMR data indicate some evidence for a monomer dimer equilibrium [47]. The variable-temperature ^{119}Sn NMR spectra of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ show a large downfield shift of 2315 ppm at 100 °C attributable to the monomer, and at –108 °C two signals are seen at higher field which have been attributed to different conformations of the dimeric species [48].

The solid state variable-temperature ^{119}Sn and ^{13}C NMR spectra of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ together with the solution spectra are all consistent with a monomer–dimer equilibrium, the energy of dissociation being calculated as 53.5 kJ mol^{–1}. The small dissociation energy and the low $^1J(^{119}\text{Sn}–^{117}\text{Sn})$ of 1340 ± 10 Hz both suggest that in the dimer the bonding between the tin atoms is best described as a weak dative interaction, and not a covalent double bond [48].

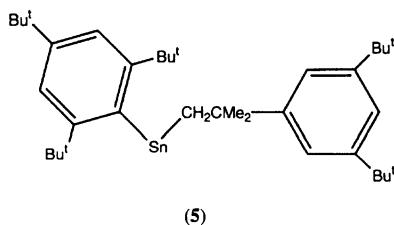
Electron diffraction data show $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ to be a V-shaped monomer in the gas phase with a C–Sn–C angle of 97(2)° and a Sn–C bond length of 2.22(2) Å [20, 49]. He(I) photoelectron spectra of R_2Ge , R_2Sn and R_2Pb [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$] have been recorded [50] and the first ionization potential was found to be close to that for the atomic metal (7.42 eV for R_2Sn) and was attributed to the lone-pair orbital on the metal. *Ab initio* MO calculations on H_2SnSnH_2 show that a *trans*-folded structure (as is found experimentally for $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$) is more stable than a planar structure. These calculations also give an Sn–Sn distance of 2.71 Å and an Sn–Sn dissociation energy of 90 kJ mol^{–1} [46, 51]. MNDO calculations by Dewar *et al.* also predict the *trans*-folded to be the preferred structure for H_2SnSnH_2 [52]. The crystal structure of $[(\text{PPh}_2)_2\text{CH}]_2\text{Sn}$ shows the compound to be monomeric and to have a pyramidal $[\text{SnCP}_2]$ core [39].

The two-coordinate monomeric dialkylstannylene (**1**) is structurally similar to $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$. It appears to be monomeric in benzene solution as evidenced by the ^{119}Sn NMR chemical shift of 2323 ppm which is close to the value of 2315 ppm for $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ in dilute solution. X-ray crystallography also shows the stannylene to be monomeric, the shortest Sn···Sn distance being 7.14 Å, and that there are no short intramolecular interactions. The decrease in flexibility, and the cyclic nature of the stannylene are probably both factors that favour the monomeric structure over the dimeric nature of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ [22].

The dimer of the stannylene (2-Bu[–]-4,5,6-Me₃C₆H)₂Sn has an Sn···Sn distance of 2.910(1) Å, i.e. longer than a typical single bond Sn–Sn distance of 2.78 Å, but still much shorter than the distances found in the monomeric stannylenes. The dimer has a *trans*-bent structure but it is unsymmetrical, the

sum of the angles at one tin being 354.9° and the other 320.9° , giving fold angles of 21.4 and 64.4° . The ^{119}Sn NMR chemical shift for a benzene solution of the stannylene varies from 1401 to 1331 ppm on changing the temperature from 373 to 298 K [30]. Although in the solid-state structure of $[2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ there are no short $\text{Sn}\cdots\text{Sn}$ interactions, there are short (2.67 – 2.82 Å) intramolecular $\text{Sn}\cdots\text{F}$ interactions between the tin and some of the *ortho* fluorine atoms. The intramolecular $\text{Sn}\cdots\text{F}$ interactions persist in solution and ^{119}Sn NMR spectroscopy shows $J(^{119}\text{Sn}-^{19}\text{F})$ of 239.5 Hz. The $2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2$ group is probably thus effective in stabilizing the stannylene by both steric protection and by the electron donating ability of the fluorine lone pairs [28]. A second crystal modification of $[2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ is formed as red crystals if the yellow material formed on initial synthesis is sublimed. The red material appears to be a thermodynamically controlled product and the yellow kinetically controlled. The second modification is a stannylene dimer with a long (3.639 Å) tin–tin interaction [53].

The stannylene $(2,4,6\text{-Bu}^t\text{C}_6\text{H}_2)_2\text{Sn}$ is clearly monomeric in the solid state; there are no $\text{Sn}\cdots\text{Sn}$ distances less than 8.84 Å and there seem to be no significant intramolecular $\text{Sn}\cdots\text{C}$ or $\text{Sn}\cdots\text{H}$ interactions. In solution the ^{119}Sn NMR spectrum shows two signals rather than the expected single peak. This is due to an isomerization of one of the aryl groups to give the less hindered stannylene (5). The ^{119}Sn NMR chemical shifts, 961 and 1105 ppm, are similar to each other but quite distinct from the range found for other monomeric R_2Sn species, i.e. 2200 – 2400 ppm [29, 54].



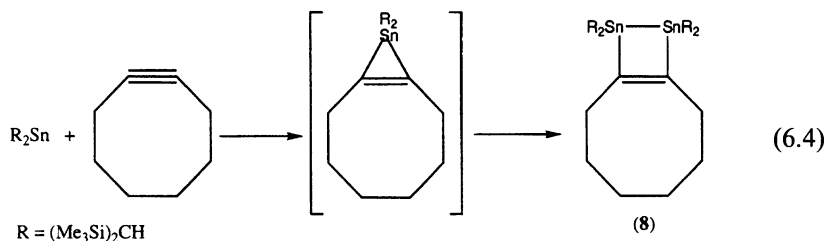
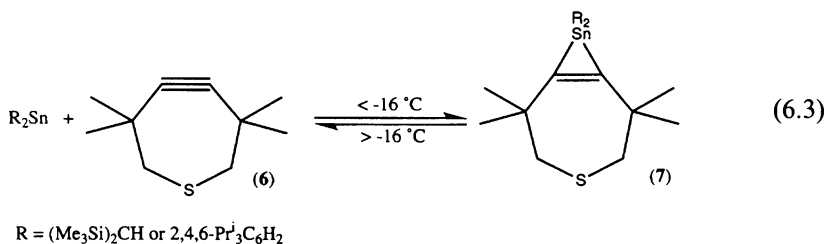
The four-coordinate $(o\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{Sn}$, has a structure comprising a distorted trigonal bipyramid, the lone pair occupying an equatorial position with Sn-N distances of $2.516(3)$ and $2.660(3)$ Å and Sn-C distances of $2.216(3)$ and $2.227(3)$ Å [33].

6.2.3 Reactions

Unless the R group in R_2Sn of alkyl or arylstannylenes is bulky, their dominant reaction is rapid oligomerization [1]. Calculations [45] on the insertion reactions of Me_2Sn with Me_2SnCl_2 , Me_3SnCl and MeI predict concerted mechanisms for reaction with Me_2SnCl_2 and Me_3SnCl but a two-step mechanism via $\text{CH}_3\cdot$ and $\text{Me}_2\text{ISn}\cdot$ for the reaction with MeI . These calculations agree qualitatively with experimental results.

Bis[bis(trimethylsilyl)methyl]tin(II) does not form adducts with Lewis acids such as BF_3 , but does undergo oxidative-addition reactions with a wide variety of organic compounds including alkyl halides, aryl halides, halogens, dienes, ketones, aldehydes, acid chlorides and with the organoboron compound $(\text{Me}_3\text{Si})_2\text{C}(\text{BBu}^t)_2\text{C}$ to form the first structurally characterized compound containing a $\text{Sn}=\text{C}$ bond [55–58]. A radical mechanism involving $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{XSn}$ as an intermediate ($\text{X}=\text{halogen}$) has been proposed for the reactions with alkyl and aryl halides [56]. 1,2-Diketones react faster than vinyl carbonyl compounds which in turn react faster than 1,3-dienes. A polymer containing alternating $\text{Sn}(\text{IV})$ and *p*-hydroquinone units can be obtained from the reaction between $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ and *p*-benzoquinone [59].

It is possible to obtain reaction products derived from addition of either one or two $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ units in reactions with $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ although products containing only one tin atom predominate. In the reaction of the cyclic acetylene (6) with $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ the tin compound acts as a monomeric stannylenes and gives a [2 + 1] cycloaddition product, the stannacyclopentene (7) as a pale yellow solid (eqn 6.3) [60–61]. A similar product is formed if $(2,4,6\text{-Pr}^i_3\text{C}_6\text{H}_2)_2\text{Sn}$ (derived from the analogous cyclotristannane) reacts with (6) [61]. Reaction of $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ with cyclooctyne proceeds slowly at room temperature to give the 1,2-distannacyclobut-3-ene derivative (8) as an air-stable white crystalline solid (eqn 6.4). The reaction is thought to proceed via initial formation of a stannacyclopentene by reaction of R_2Sn with the alkyne, followed by stannylenes insertion into the $\text{Sn}-\text{C}$ bond of the three-membered ring [62].



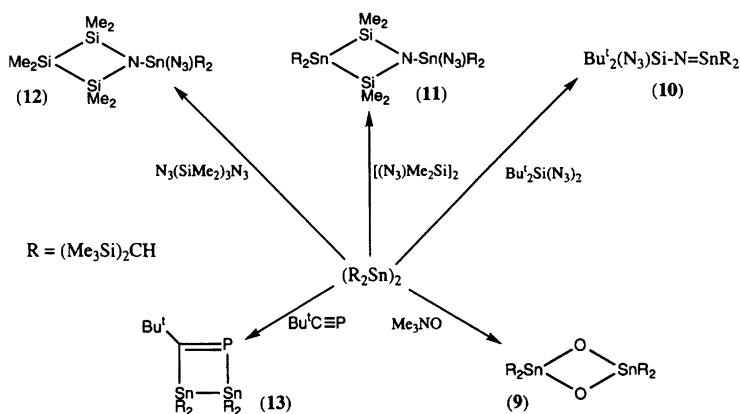
The stannylenes $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$ also reacts with a variety of Group 15 reagents to give novel cyclic products. The reaction with Me_3NO affords the

novel cyclodistannoxane (**9**) [63], the reaction with $\text{Bu}'_2\text{Si}(\text{N}_3)_2$ gives the stannaimine (**10**) and reactions with diazidosilanes $[(\text{N}_3)\text{Me}_2\text{Si}]_2$ and $\text{N}_3(\text{SiMe}_2)_3\text{N}_3$ give (**11**) and (**12**), respectively (Scheme 6.1) [64]. The reaction with $\text{Bu}'\text{C}\equiv\text{P}$ gives the phosphadistannacyclobutene (**13**), apparently via a $[2+2]$ cycloaddition pathway rather than sequential addition of R_2Sn units (Scheme 6.1) [65].

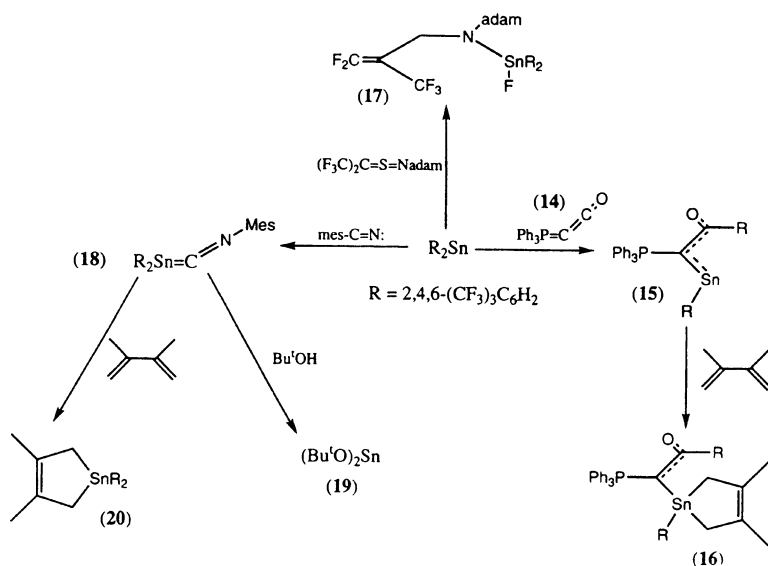
Reaction of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ with a sodium mirror at low temperature gives the radical anion $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}^{\cdot-}$, the ESR spectrum of which shows a small hyperfine coupling constant $a(^{117,119}\text{Sn})$ indicative of the p -character attributed to the radical [66].

The increased recent interest in diarylstannylenes has led to several investigations into their reactions, mainly additions to unsaturated species. The reaction of $[2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ with the cumulene (**14**) results in formation of (**15**) in which the tin atom is two-coordinate, the $\text{Sn}-\text{Ar}$ bond of $2.25(2) \text{ \AA}$ being normal for an $\text{Sn}-\text{C}$ single bond but the other bond to tin of 2.12 \AA lies between the expected single and double tin-carbon bond lengths. With 2,3-dimethylbutadiene a $[1+4]$ cycloaddition occurs to give (**16**) (Scheme 6.2) [67]. Reaction of the stannylene with $(\text{CF}_3)_2\text{C}=\text{S}=\text{N}(\text{adamantyl})$ gives the tin(IV) product (**17**) which has been characterized by X-ray crystallography [68]. Reaction of the diarylstannylene with mesitylisocyanide gives the stannaketenimine (**18**) which has a bent geometry with an $\text{Sn}-\text{C}-\text{N}$ angle of $153.9(2)^\circ$. A subsequent reaction with $\text{Bu}'\text{OH}$ or 2,3-dimethylbutadiene gives products (**19**) and (**20**), respectively (Scheme 6.2), which are also the products from the reactions of the stannylene with these reagents [69].

Reaction of $[2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ with mesitylazide leads to the loss of N_2 and the formation of the cycloaddition product, the azadistanniridine (**21**). In toluene solution at 60°C the three-membered ring breaks down to give the stannylene and the stannaimine which then either dimerizes or, in the presence of excess azide, gives the five-membered ring product (**22**) (Scheme



Scheme 6.1

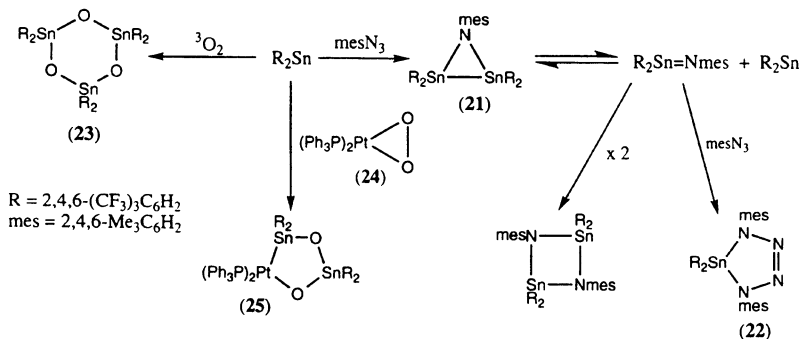


Scheme 6.2

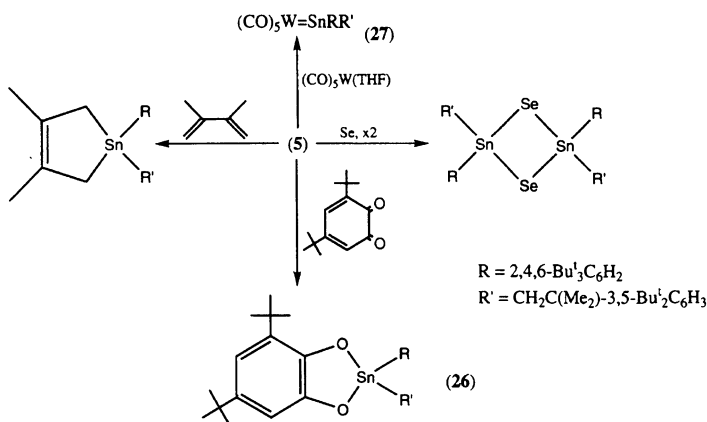
6.3) [70]. Reaction of the arylstannylene with triplet oxygen gives the cyclotristannoxane (23) but with the platinum complex (24) an unusual five-membered heterocycle (25) is formed (Scheme 6.3) [71].

The stannylene (2- Bu^t -4,5,6- Me_3C_6H) $_2Sn$ can be trapped in solution by 3,5-di-*tert*-butylbenzoquinone to give a [4 + 1] cycloadduct analogous to (26) [30] and bis(2,6-bis(trifluoromethyl)phenyl)tin(II) reacts with methanol and *p*-toluenethiol to give [2,6- $(CF_3)_2C_6H_3$] $SnOMe$ and (4- MeC_6H_4S) $_2Sn$, respectively [27]. Stannylene (5) forms only in solution but it can be derivatized with a range of reagents as shown in Scheme 6.4, and the products isolated and characterized [54].

The very bulky stannylene (2) reacts with a variety of unsaturated and sulphur or selenium-containing substrates to give a range of mainly cyclic products (Scheme 6.5) [31, 32, 72].



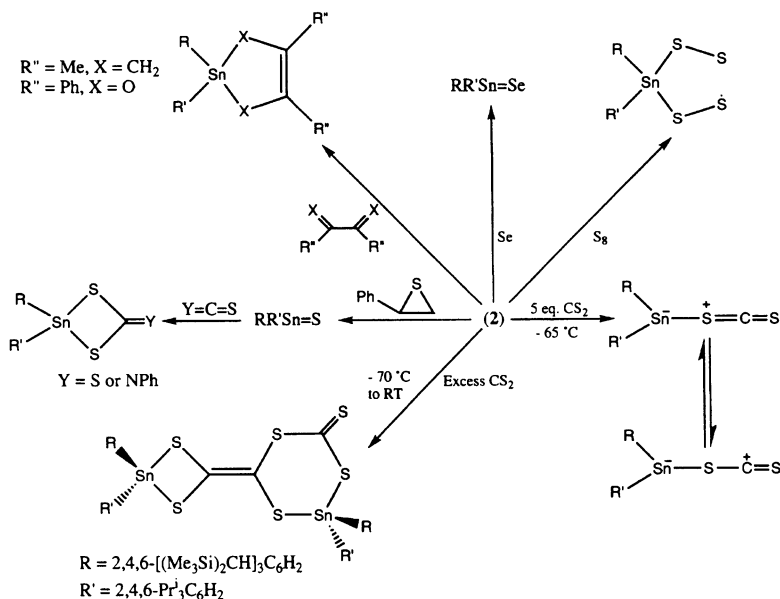
Scheme 6.3



Scheme 6.4

6.2.4 Transition metal complexes

An organometallic tin(II) species can act in transition metal complexes either as a terminal or bridging ligand, or as a terminal ligand with one or more bases also coordinated to the tin atom. The bonding in complexes with a terminal tin(II) ligand can be considered to be similar to that in carbene complexes with σ -donation from the tin to the transition metal and back donation from the transition metal to the empty p - or d -orbitals of the tin. In the base-complexed terminal complexes, the tin also functions as a Lewis

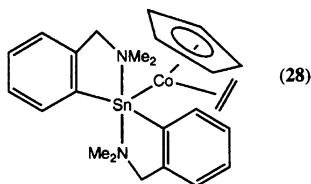


Scheme 6.5

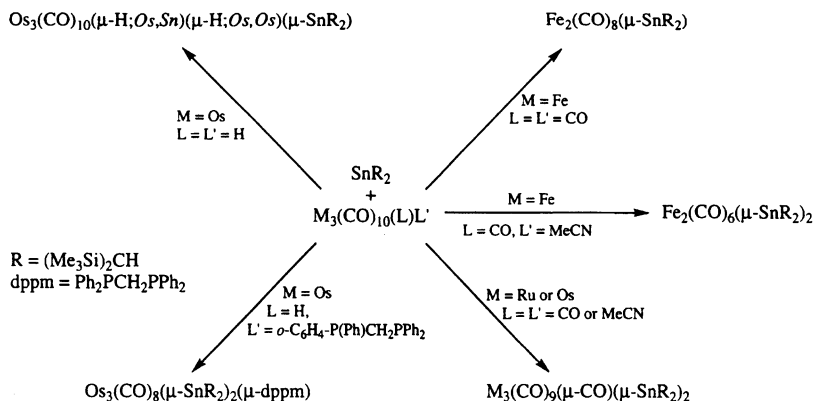
acid and there is additional coordination of a base by the vacant *p*-orbital of the tin, while in the bridged complexes the tin(II) ligand bridges between two transition metals.

Terminal complexes containing alkyl- or aryltin(II) derivatives appear to be restricted to those complexes of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ (R_2Sn). The stannylene $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ can displace CO or R_3P from transition metal complexes and also inserts into M–M, M–alkyl and M–H bonds. The monostannylene complexes $[\text{M}(\text{CO})_5\text{SnR}_2]$ ($\text{M}=\text{Cr}$ or Mo) were obtained in 43 and 64% yields respectively by UV irradiation of hexane solutions of R_2Sn and $\text{M}(\text{CO})_6$ [55]. The crystal structure of $[\text{Cr}(\text{CO})_5\text{SnR}_2]$ [73] showed the $(\text{Me}_3\text{Si})_2\text{CH}$ carbons, and the chromium and tin atoms to be coplanar with an Sn–Cr bond length of 2.562 Å. A compound containing a terminally bound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ ligand on a triosmium cluster has been prepared which has a Sn–Os distance of 2.573 Å, rather shorter than is found for terminally bound R_3Sn –Os distances [74]. Complexes containing bridging R_2Sn ligands can be prepared from carbonyltrimetallallic clusters of Fe, Ru or Os (Scheme 6.6) [74–77].

The four-coordinate (*o*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CH}_2$) $_2\text{Sn}$ reacts with $\text{CpCo}(\eta^2\text{-C}_2\text{H}_4)_2$ to give the new stannylene complex (28) as red crystals with an Sn–Co distance



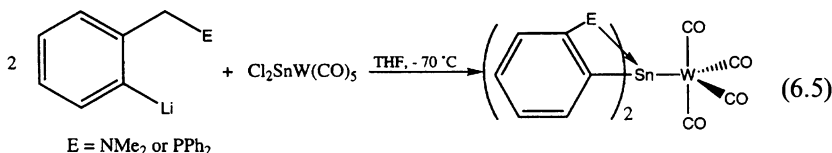
of 2.438(1) Å [33]. The tungsten complex (27) is pale yellow and has a planar geometry at tin. The C–Sn–C angle of 91.5° is relatively small, which presum-



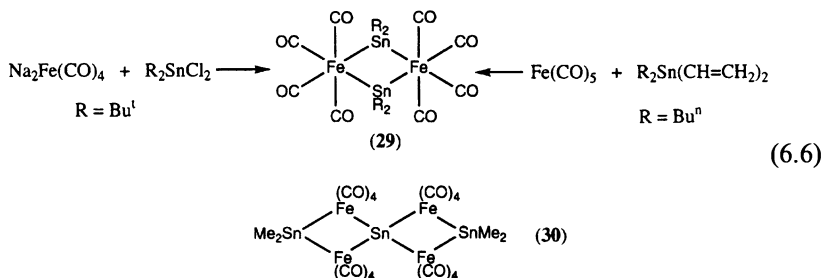
Scheme 6.6

ably reflects the lower degree of steric bulk provided by the alkylaryl substitution, and the $W=Sn$ distance is $2.751(1) \text{ \AA}$ [54].

Terminal complexes containing Me_2Sn , Bu_2Sn and Ph_2Sn with a base such as THF or pyridine coordinated to the tin can be prepared in solution either by dissolving a bridged dimer in a coordinating solvent, or by treating dialkyldichlorostannanes with $Na_2Cr_2(CO)_{10}$ in the presence of a Lewis base [78, 79]. On removal of solvent only the bridged dimers are recovered using THF as base, but with the more basic pyridine, the complex $[(CO)_4Fe(SnBu_2) \cdot \text{pyridine}]$ can be isolated in 88% yield as an orange-brown solid [80]. The crystal structure of the relatively stable chromium complex $[(CO)_5Cr(SnBu_2) \cdot \text{pyridine}]$ [81] showed that the tin was tetracoordinated with an $Sn-Cr$ distance of 2.654 \AA , i.e. 0.092 \AA shorter than that in the terminal complex $\{(CO)_5CrSn[CH(SiMe_3)_2]\}$. Base-stabilized arylstannylene ligands have been prepared in which the basic donor atoms are substituents on the aryl rings and there is intramolecular coordination by two basic atoms making the tin penta-coordinated. Thus, in eqn 6.5 the products are formed in 61 and 42% yields, for $E=NMe_2$ and PPh_2 , respectively, in which the $W-Sn$ distances are 2.749 and 2.762 \AA , respectively [82, 83].



Compounds in which a stannylene bridges two metals have been prepared by several methods. For example, treatment of Bu_2SnCl_2 with $Na_2Fe(CO)_4$ (eqn 6.6) affords a golden-yellow dimer in 50% yield [80] and treatment of $Bu_2Sn(CH=CH_2)_2$ with $Fe(CO)_5$ affords a yellow dimer in 28.5% yield [84]. The crystal structures of (29) ($R=Me$) and (30) [both products from the reaction between $MeSnCl_3$ and $Na_2Fe(CO)_4$] have been determined [85, 86] and have $Sn-Fe$ bond lengths of 2.625 (terminal Sn) and 2.647 \AA , respectively and $Fe-Sn-Fe$ angles of 105.2 (terminal) and 77° respectively.

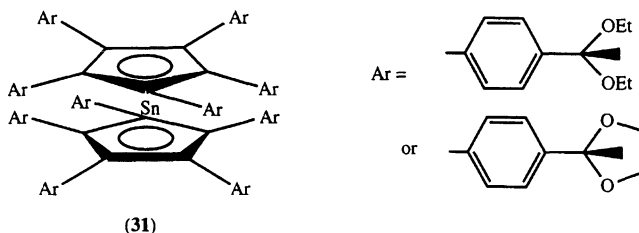


6.3 π -Bonded complexes

6.3.1 Synthesis

The chemistry of π -bonded organometallic complexes of bivalent tin dates back to the first preparation of bis(cyclopentadienyl)tin (stannocene) from the reaction between SnCl_2 and two equivalents of NaCp in 1956 [87]. The same salt elimination method using SnCl_2 and an alkali metal salt of a cyclopentadiene derivative has been used extensively to prepare substituted stannocenes such as $(\text{Bu}'\text{C}_5\text{H}_4)_2\text{Sn}$ [88], $(\text{Bz}_5\text{C}_5)_2\text{Sn}$ [89], $(\text{Ph}_5\text{C}_5)_2\text{Sn}$ [90, 91], $(\text{CH}_2=\text{CMeC}_5\text{H}_4)_2\text{Sn}$ [92], $(\text{Me}_5\text{C}_5)_2\text{Sn}$ [93, 94], $(\text{MeC}_5\text{H}_4)_2\text{Sn}$ [95], $[(\text{Me}_3\text{Si})_n\text{C}_5\text{H}_{5-n}]_2\text{Sn}$ ($n=2$ or 3) [96], *ortho*-, *meta*- or *para*- $\text{C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_4)_2\text{Sn}$ [97] and the bridged $(\text{CH}_2\text{SiMe}_2\text{C}_5\text{Me}_4)_2\text{Sn}$ [98]. More recent work has investigated the use of other highly substituted ligands in attempts to make air-stable compounds. A review of the use of bulky cyclopentadienyl ligands in organometallic chemistry, including tin compounds, was published in 1991 [99]. The highly alkylated stannocenes $[(\text{Pr}^i)_{5-n}\text{C}_5\text{H}_n]_2\text{Sn}$ ($n=1$ or 2) are formed in the reaction between the appropriate potassium cyclopentadienide derivatives and SnCl_2 in THF solution. The octa-substituted compound is an air-stable pale yellow solid and the hexa-substituted compound an air-sensitive deep yellow oil [100]. Reaction of $1,3\text{-Bu}'_2\text{C}_5\text{H}_3\text{Li}$ with SnCl_2 gives a 69% yield of cream coloured crystals of $(1,3\text{-Bu}'_2\text{C}_5\text{H}_3)_2\text{Sn}$ which, when treated with HBF_4 , affords $(1,3\text{-Bu}'_2\text{C}_5\text{H}_3)\text{SnBF}_4$ as colourless crystals. ^1H and ^{13}C NMR data for the BF_4 salt suggest that it has a half-sandwich structure [101]. Reaction of SnCl_2 with $\text{Ph}_4\text{HC}_5\text{Li}$ gives $(\eta^5\text{-Ph}_4\text{HC}_5)_2\text{Sn}$ as a yellow crystalline solid in 37% yield; similarly reaction of SnCl_2 with $(p\text{-Bu}'\text{Ph})\text{Ph}_4\text{C}_5\text{Li}$ gives the air-stable $[(p\text{-Bu}'\text{Ph})\text{Ph}_4\text{C}_5]_2\text{Sn}$ in 51% yield [102]. The reaction of $\text{Ph}_5\text{C}_5\text{Na}$ with CpSnCl gives the mixed ligand compound $(\text{Ph}_5\text{C}_5)\text{CpSn}$ as a pale yellow solid in 23% yield, stable in the air for a short time [91, 103].

A variety of soluble decasubstituted decaphenyl metallocenes, e.g. (31) have been prepared in good yield (using the reaction between SnCl_2 and the appropriate cyclopentadienyl anion) in which the phenyl groups are all



substituted in the *para* position. It will be of interest to investigate the electronic and structural properties of such compounds for comparison with compounds with more traditional substituents [104].

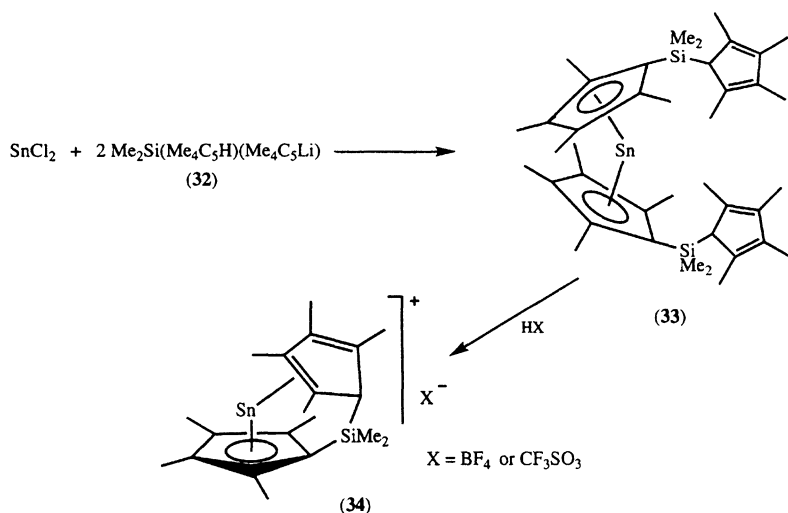
Reaction of SnCl_2 with (32) according to Scheme 6.7 gives (33) which,

when treated with HX ($X = \text{BF}_4$ or CF_3SO_3), gives the metallocenophane-like complexes (34). The X-ray structure of the BF_4 salt shows the compound to be a centrosymmetric dimer with bridging BF_4 groups, with the cyclopentadienyl ring being η^5 -bonded to the tin and the cyclopentadiene ring being bound in an η^2 fashion [105].

It is also possible to prepare substituted stannocenes without the use of alkali metal cyclopentadienide reagents. The direct reaction between tin powder and $\text{Me}_5\text{C}_5\text{Br}$ leads to initial formation of $\text{Me}_5\text{C}_5\text{SnBr}$, a second oxidative addition leading to the tin(IV) compound $(\text{Me}_5\text{C}_5)_2\text{SnBr}_2$. Both compounds are also products in the reaction between $(\text{Me}_5\text{C}_5)_2\text{Sn}$ and $\text{Me}_5\text{C}_5\text{Br}$ [106]. Decamethylstannocene has also been prepared by direct reduction of the corresponding diorganotin(IV) dihalides, $(\text{Me}_5\text{C}_5)_2\text{SnX}_2$ ($X = \text{Cl}$ or Br), with either lithium naphthalenide or dilithium cyclooctatetraenide. The best yield (70%) is obtained by using the dichloride and lithium naphthalenide [107].

Treatment of stannocene with one equivalent of SnCl_2 or SnBr_2 leads to an exchange reaction and the formation of cyclopentadienyln(II) chloride or bromide respectively [108]. Many other stannocene derivatives have been obtained by substitution at the coordinated cyclopentadienyl rings, and these are discussed in section 6.3.3.

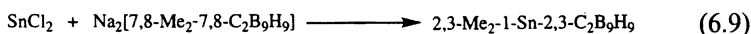
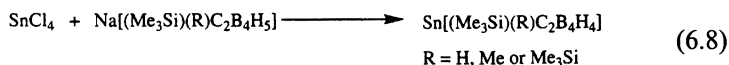
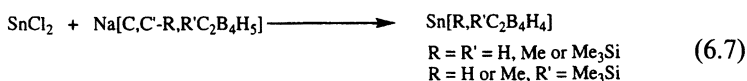
A small number of arenetin(II) complexes have been prepared as colourless, very air-sensitive crystals by reaction of SnCl_2 and AlCl_3 in the presence of the arene as solvent [109–111]. There seems to be no reaction between stannocene (or SnCl_2 or SnBr_2) and mesitylene but both $\text{Sn}(\text{SO}_3\text{F})_2$ and $\text{Sn}(\text{SbF}_6)_2$ form mesitylene adducts, $\text{Sn}(\text{SO}_3\text{F})\cdot\text{mes}$ and $\text{Sn}(\text{SbF}_6)_2\cdot 2\text{mes}$, but



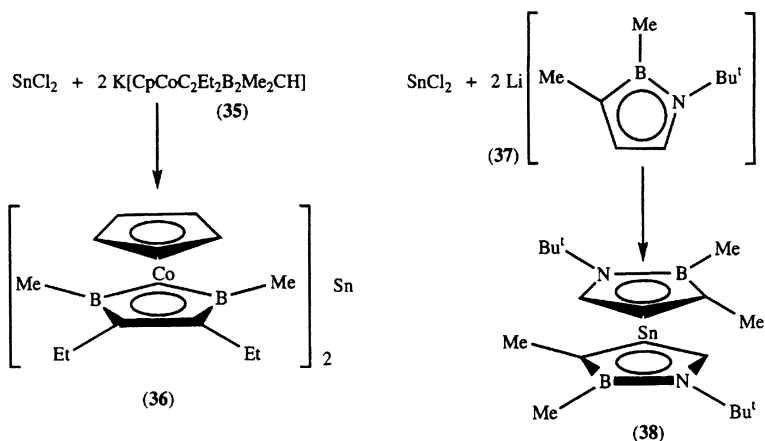
Scheme 6.7

the detailed structure of neither compound is known. Mössbauer data do, however, suggest that the arene ring does interact with tin atom in these species [112].

Several compounds in which a bivalent tin is incorporated into a carborane cage have been prepared using the salt elimination route (eqns 6.7–6.9) [113–117]. A detailed account of the chemistry and structural characteristics of Group 14 carborane derivatives has also been published [118].



The isolobal relationship between Cp^- and $\text{CpCo}(\text{C}_3\text{B}_2)^-$ has prompted the use of the 1,3-diborenyl unit as a π -ligand to tin. Hence treatment of SnCl_2 with anion (35) leads to a dark orange tetradecker sandwich compound, (36) in 69% yield (Scheme 6.8) [119]. The 1,2-azaborolynyl ligand has also been used as a π -ligand to tin, and treatment of SnCl_2 with the lithium salt (37) gives the orange-yellow stannocene-like compound (38) as a mixture of diastereomers in 49% yield (Scheme 6.8) [120]. The tetradecker compound is thermally quite stable and decomposes at 140°C but (38) decomposes with formation of tin at -20°C .



Scheme 6.8

6.3.2 Structure

AM1 parameters for tin have been described and calculations using them give the bent structure for stannocene as a minimum on the potential energy surface, unlike MNDO methods for which the D_{5d} geometry is predicted [121]. The use of MM3 force field methods enables the conformations of stannocenes, either with parallel C_5 rings or with bent sandwich structures, to be calculated correctly [122].

The first observations [87] on the structure of stannocene were that it was monomeric in benzene solution and that it had a non-zero dipole moment, which were thought to imply a σ -bonded structure. However, the true pentahapto π -bonded sandwich structures of stannocene and its derivatives have since been demonstrated in numerous ways including X-ray diffraction studies. Infrared and Raman spectra of stannocene and its derivatives have been recorded [89, 123] with IR spectroscopy being used to distinguish mono- from pentahapto bonding.

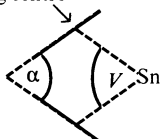
The solid-state structure of stannocene has been determined by X-ray crystallography [124] and (unlike plumbocene) is found to be monomeric with two crystallographically independent molecules in the unit cell. In contrast to ferrocene, the cyclopentadienide rings are not parallel in either molecule and have ring centroid–metal–ring centroid angles (V) of 148.0 and 143.7° for the two different molecules. The gas-phase electron diffraction structure [125] shows a smaller angle V of about 125°, but the data were poor and no detailed comparisons between the structure in the solid and gas phases can be drawn. The structure of several substituted stannocenes have also been determined and details are summarized in Table 6.1.

The ‘bent sandwich’ structure of most of the stannocene derivatives is attributed to the tin having sp^2 hybridization, with two of the hybrid orbitals interacting with the π -system of the rings and the other containing an unshared pair of electrons which, in all but the decaphenyl derivative, overcomes any steric repulsion caused by the rings. Steric factors do, however, play a role, and the data in Table 6.1 show that the larger the substituents on the rings, the nearer to being parallel they become. Care must be exercised when comparing V -angles as the ring centroid–Sn–ring centroid angle is different to that subtended by perpendiculars from the rings crossing at tin. This has led to the erroneous comment [124] that V is larger in $(C_5H_5)_2Sn$ than $(Me_5C_5)_2Sn$ but this has since been corrected and reversed [126].

The X-ray structure of $[(Pr^i)_4C_5H]_2Sn$ shows that, as usual the Cp ligands do not have a symmetrical η^5 coordination, leading to a ring centroid–Sn–ring centroid angle of 165° and the ring normal–Sn–ring normal of 152.2°. These large values highlight the considerable steric bulk that the $Pr^i_{5-n}C_5H_n$ ligands provide [100]. The X-ray structure of a toluene solvate of $(Ph_5C_5)(Cp)Sn$ shows the molecule to be bent, the angle between the two C_5

Table 6.1 Structural data for stannocenes and related species

Compound	Method	$\alpha(^{\circ})^c$	$V(^{\circ})^c$	Ref.
$(C_5H_5)_2Sn$	X-ray	48.4 45.9	148.0 143.7	124, 126 124, 126
$(C_5H_5)_2Sn$	e.d. ^b	~55	~125	125
$(MeC_5H_4)_2Sn$	e.d. ^b	34±7		126
$(Me_5C_5)_2Sn$	X-ray	36.4 35.4	154.9(2) 154.8(2)	94, 103 94, 103
$(Bz_5C_5)_2Sn$	X-ray	32.8(2)	155.89(9)	89
$[1,2,4-(Me_3Si)_3C_5H_2]_2Sn$	X-ray	16(4)	162±2	96, 103
$\{[(Pr^i)_4C_5H]_2Sn$	X-ray		165	100
$(Ph_5C_5)_2Sn$	X-ray	0	180	90
$(Ph_5C_5)(C_5H_5)Sn$	X-ray	43.9(3)	151.1(1)	103
$\{[(Pr^i)_2N]_2PC_5H_4\}_2Sn$	X-ray		150.2	127
$\{[BF_4](C_5H_5)_2Sn[C_5H_5Sn]\}^+THF\}$	X-ray		138.7 ^a	128
$[Bu^iNB(Me)(CH)_3CMe]_2Sn$	X-ray	46.5		120
$[(C_5H_5)CoBMe(CEt)_2BMeCH]_2Sn$	X-ray	68.66		119
$(C_5H_5)SnCl$	X-ray		117.4	103

^aIn the $(C_5H_5)_2Sn$ moiety.^bGas-phase electron diffraction.^c ring centre

rings being less than that in $(Ph_5C_5)_2Sn$ or $(Me_5C_5)_2Sn$ but greater than that found for Cp_2Sn or $(MeH_4C_5)_2Sn$ (Table 6.1) [103].

The 1H and ^{13}C NMR spectra of $(MeC_5H_4)_2Sn$, $(MeC_5H_4)_2Ge$ and $(MeC_5H_4)_2Pb$ are found to be quite similar [95], suggesting similar sandwich structures. Coupling between Sn and C or H in $(MeC_5H_4)_2Sn$ was not observed at ambient temperature, but at $-55^{\circ}C$ and $-40^{\circ}C$, coupling of 1H to ^{119}Sn was observed, this being consistent with rapid intermolecular exchange at higher temperatures. Substituted cyclopentadienyl ligands seem to slow down intermolecular exchange and coupling to ^{119}Sn is observed for $(Me_5C_5)_2Sn$ and $(Me_5C_5)SnBF_4$ at ambient temperatures. The ^{119}Sn NMR chemical shifts for stannocene derivatives are shifted more than 2100 ppm upfield from the usual position for Sn(IV) species, which can be attributed to shielding caused by increased *s*-electron density at the tin nucleus. The He(I) [129, 130] and He(II) [130] photoelectron spectra of $(Me_5C_5)_2Sn$ and the He(I) and He(II) [129, 131] spectra of $(C_5H_5)_2Sn$ have been recorded. The lowest ionization potential for $(C_5H_5)_2Sn$ is at 7.57 eV and has been attributed to electron loss from the C_5H_5 ring [129]. In $(Ph_5C_5)_2Sn$, which is bright yellow and has S_{10} molecular symmetry, the lone pair is stereochemically inert.

A solid state (CP-MAS) ^{119}Sn NMR study of $(Me_5C_5)_2Sn$ shows two tin chemical shifts, only a few ppm apart, in good agreement with the X-ray structure which shows two slightly different molecules in the unit cell. The

chemical shifts in the solid state are close to that found in solution which suggests that the structures in the solid state and in solution are similar [132]. A similar solid-state NMR study of Cp_2Sn is also in agreement with the X-ray structural data, again showing two different tin environments. The mean of the solid-state chemical shift values is also close to the value in solution, again consistent with the solid and the solution structures being similar. The reaction between Cp_2Sn and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ in benzene solution leads to an equilibrium being set up between the two symmetrical starting materials and $\text{CpSnN}(\text{SiMe}_3)_2$. The ^{119}Sn chemical shift of the mixed ligand species lies, as might be expected, about halfway between those of the symmetrical compounds [133]. Solid-state ^{119}Sn NMR spectroscopy gives chemical shifts of -2288 , -2215 , -2210 and -2235 ppm for $(\text{Bz}_5\text{C}_5)_2\text{Sn}$, $(\text{Ph}_5\text{C}_5)_2\text{Sn}$, $(\text{Ph}_4\text{HC}_5)_2\text{Sn}$ and $[(\text{Bu}'\text{Ph})\text{Ph}_4\text{C}_5]_2\text{Sn}$ respectively [91].

The two sets of phenyl rings in $(\text{Ph}_5\text{C}_5)_2\text{Sn}$ are almost perpendicular to each other; this was found to be the lowest energy conformation by molecular modelling [134]. Fenske–Hall MO calculations for $(\text{Ph}_5\text{C}_5)_2\text{Sn}$ predict that the tin lone pair is not delocalized into the ligand ring systems but is in a tin $5s$ -like orbital [134]. The crystal structures of the salts $(\text{Bu}'\text{C}_5\text{H}_4)\text{Sn}^+\text{BF}_4^-$ [135], $\text{C}_5\text{Me}_5\text{Sn}^+\text{BF}_4^-$ [94, 136] and $\text{C}_5\text{H}_5\text{Sn}^+\text{Cl}^-$ [137] show that the tin atom lies above the centre of the ring with an average $\text{Sn}-\text{C}_{\text{ring}}$ distance of 2.462 \AA , somewhat shorter than that found in $(\text{Me}_5\text{C}_5)_2\text{Sn}$ (2.585 – 2.770 and 2.567 – 2.767 \AA in the two crystallographically distinct molecules [94]) indicating a stronger interaction between the ring and the tin in the $[\text{C}_5\text{Me}_5\text{Sn}^+]$ cation than in the neutral $(\text{Me}_5\text{C}_5)_2\text{Sn}$. In both $(\text{Bu}'\text{C}_5\text{H}_4)\text{Sn}^+\text{BF}_4^-$ and in $\text{C}_5\text{H}_5\text{Sn}^+\text{Cl}^-$ the tin atom is not above the ring centre with $\text{Sn}-\text{C}_{\text{ring}}$ distances of 2.443 – 2.559 and 2.45 – 2.74 \AA , respectively, $\text{C}_5\text{H}_5\text{Sn}^+\text{Cl}^-$ having a ring centroid– $\text{Sn}-\text{Cl}$ angle of 117.4° .

Extended Huckel calculations predict the HOMO for $\text{C}_5\text{H}_5\text{Sn}^+\text{BF}_4^-$ to be a tin lone pair [94], however, MNDO calculations, which are probably more reliable for calculation of ionization energies, predict a pair of nearly degenerate HOMOs localized on the ring to lie above the tin lone pair [52]. Jutzi *et al.* have also prepared N-donor complexes of $\text{Me}_5\text{C}_5\text{Sn}^+$ cations by treating $\text{Me}_5\text{C}_5\text{Sn}^+\text{CF}_3\text{SO}_3^-$ with various aromatic amines [138, 139]. The X-ray crystal structures of $[\text{Me}_5\text{C}_5\text{Sn-amine}]^+[\text{CF}_3\text{SO}_3]^-$ (amine = pyridine or 2,2'-bipyridine) have been determined and show that amine coordination distorts the bonding between the Me_5C_5 and the tin from η^5 towards η^2 or η^3 with $\text{Sn}-\text{N}$ distances of about 2.62 and 2.48 \AA in the pyridine and 2,2'-bipyridine complexes, respectively.

Although the 1,3-diborolenyl ligands in (36) (Scheme 6.8) interact with the tin in an essentially pentahapto fashion, in (38) (Scheme 6.8) the tin atom is displaced in the direction of the CCB ring fragment and away from the nitrogen suggesting a trihapto interaction. The X-ray crystal structures of several of the stannacarboranes mentioned in the previous section have been determined by X-ray crystallography. Both $\text{Sn}(\text{Me}_3\text{Si})(\text{Me})\text{C}_2\text{B}_4\text{H}_4$ [114] and

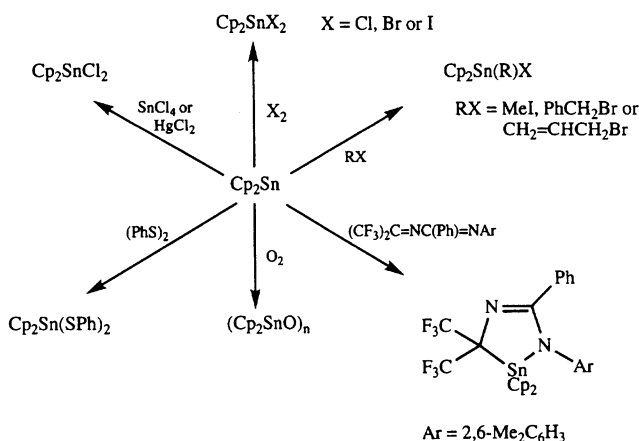
$\text{Sn}(\text{Me}_3\text{Si})\text{C}_2\text{B}_4\text{H}_5$ [140] show the tin atom to be at an apex of a distorted pentagonal bipyramid and can be regarded as being η^5 -bonded to the $[\text{C}_2\text{B}_3]$ face, with slightly longer bonds to carbon than to boron. The ^1H , ^{11}B , ^{13}C and ^{29}Si NMR spectra for the stannacarboranes $\text{Sn}(\text{Me}_3\text{Si})(\text{R})\text{C}_2\text{B}_4\text{H}_4$ ($\text{R} = \text{Me}_3\text{Si}$, Me or H) have been recorded and are all consistent with the proposed structures [115]. Coordination of the tin atoms in these compounds by 2,2'-bipyridine results in 'slippage' of the tin away from the carbon atoms in the $[\text{C}_2\text{B}_3]$ ring, and it becomes essentially η^3 -bonded to the three borons and interacts only weakly with the carbons [114, 140, 141]. A similar although less pronounced distortion also occurs when $\text{Sn}(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4$ is treated with 2,2'-bipyrimidine to give a red complex in which the bipyrimidine bridges between two $\text{Sn}(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4$ units [142].

Three arenetin(II) complexes have also been structurally characterized. In both $(\eta^6\text{-arene})\text{SnCl}(\text{AlCl}_4)$ (arene = C_6H_6 or $p\text{-Me}_2\text{C}_6\text{H}_4$) complexes the ring is unsymmetrically bound to the tin atom with $\text{Sn}-\text{C}_{\text{ring}}$ distances ranging from 2.92–3.27 and 3.05–3.339 Å when the arene is C_6H_6 or $p\text{-Me}_2\text{C}_6\text{H}_4$, respectively, i.e. much longer than those found in $\text{C}_5\text{H}_5\text{Sn}^+\text{Cl}^-$ (2.45–2.74 Å). Each tin is also part of a planar $[\text{Sn}_2\text{Cl}_2^{2+}]$ dimeric unit and is chelated by two chlorines of one AlCl_4^- unit and also one chlorine from a second AlCl_4^- unit leading to the formation of a chain structure [110, 111]. In the structure of $(\eta^6\text{-C}_6\text{H}_6)\text{Sn}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$ [109, 143], the tin is coordinated by three pairs of chlorines from three different $[\text{AlCl}_4^-]$ units and interacts fairly symmetrically with one benzene ring with an average $\text{Sn}-\text{C}_{\text{ring}}$ distance of 3.06 Å again forming a chain structure. The second molecule of benzene lies in a cleft position between the chains and is not bound to the tin.

6.3.3 Reactions

The reactions of stannocene and its derivatives can be broadly divided into two types: those of an oxidative addition nature where the $\text{Sn}(\text{II})$ is oxidized to $\text{Sn}(\text{IV})$, and those where the oxidation state of the tin remains unchanged. These will be discussed separately below.

Oxidative addition-type reactions. Although solid stannocene does not polymerize spontaneously at room temperature, it is slowly polymerized by DMF to the tetravalent $\{\text{Sn}(\text{C}_5\text{H}_5)_2\}_n$ a reaction [144] which can be regarded as an oxidative addition. The degree of substitution of the cyclopentadienyl rings plays an important role in the reactivity of substituted stannocenes. Hence, whilst stannocene itself reacts rapidly with atmospheric oxygen, $(\text{Me}_5\text{C}_5)_2\text{Sn}$ is stable in air for several hours and $(\text{Bz}_5\text{C}_5)_2\text{Sn}$ is air-stable. It has been suggested that, like the oxidative addition reactions of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$, the reaction of stannocene with MeI is also a free radical process as it does not occur in the dark [145]. Several other oxidative addition reactions of stannocenes are known and some are summarized in Scheme 6.9 [93, 144-]



Scheme 6.9

147]. Reaction of $(\text{C}_5\text{H}_5)_2\text{Sn}$ with the ylide $\text{CH}_2=\text{PF}(\text{NMe}_2)_2$ in refluxing toluene leads to the formation of a new ylide containing a cyclopentadiene ring, but the fate of the tin is unclear [148].

Non-oxidative reactions. Stannocene and its derivatives can undergo reactions in which either one or both rings are lost. A single ring can be displaced by a variety of reagents such as $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$, Ph_3CBr or RCO_2H to give compounds of type $\text{C}_5\text{H}_5\text{SnX}$ ($\text{X}=(\text{Me}_3\text{Si})_2\text{N}$, Br , CF_3 or CCl_3) [145, 149, 150]. Salts are formed if a relatively weakly nucleophilic anion is available, for example, reaction of $(\text{Me}_5\text{C}_5)_2\text{Sn}$ with $\text{CF}_3\text{SO}_3\text{R}$ ($\text{R}=\text{H}$ or Me), AlCl_3 , HBF_4 or $\text{HC}_5(\text{CO}_2\text{Me})_5$ gives $[\text{C}_5\text{Me}_5\text{Sn}]^+\text{X}^-$ (where $\text{X}=\text{CF}_3\text{SO}_3$, AlCl_4 , BF_4 or $\text{C}_5(\text{CO}_2\text{Me})_5$, respectively) and $(\text{Bu}'\text{C}_5\text{H}_4)_2\text{Sn}$ reacts with BF_3 to give $[\text{Bu}'\text{C}_5\text{H}_4\text{Sn}]^+\text{BF}_4^-$ [94, 135, 136, 150, 151]. A similar reaction is undergone by the tetradecker sandwich compound (36) (Scheme 6.8), which forms the salt $[\text{CpCoBMe}(\text{CEt})_2\text{BMeCHSn}]^+\text{BF}_4^-$ on treatment with HBF_4 [119].

Stannocene was originally thought to form a donor-acceptor complex, $(\text{C}_5\text{H}_5)_2\text{Sn}\cdot\text{BF}_3$, when treated with $\text{BF}_3\cdot\text{THF}$ [152] but a crystal structure determination [128] has shown this to be incorrect. Rather, the product has a complicated polymeric structure represented by $\{[\text{BF}_4]^- \{(\mu\text{-}\eta^5\text{C}_5\text{H}_5)_2\text{Sn}[\mu\text{-}\eta^5\text{C}_5\text{H}_5\text{Sn}]^+\text{THF}\}_n$. Stannocene does, however, form 1:1 adducts with BBr_3 , AlCl_3 and AlBr_3 [153]. An anionic tetrakis(cyclopentadienyl)tin(II) species has been prepared by treating stannocene with Me_5Sb to give the spontaneously flammable $[\text{Me}_4\text{Sb}]^{2+}[(\text{C}_5\text{H}_5)_4\text{Sn}]^{2-}$; however, its structure is unknown [154].

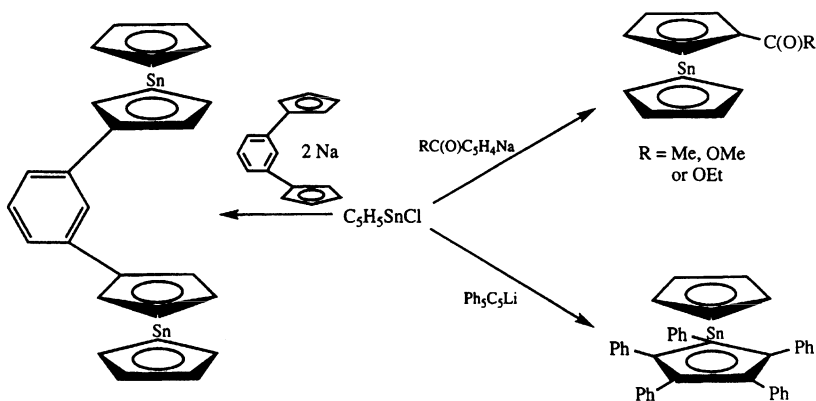
The chloride in $\text{C}_5\text{H}_5\text{SnCl}$ can be displaced using sodium or lithium reagents to afford unsymmetrical stannocenes. The mono-substituted acetyl- and alkoxycarbonyl- stannocenes $\text{C}_5\text{H}_5\text{SnC}_5\text{H}_4\text{C}(\text{O})\text{R}$ ($\text{R}=\text{Me}$, OMe or OEt) can be prepared from $\text{C}_5\text{H}_5\text{SnCl}$ and $\text{RC}(\text{O})\text{C}_5\text{H}_5\text{Na}$ in very good yields [155].

Attempts to make symmetrically substituted $[\text{RC}(\text{O})\text{C}_5\text{H}_5]_2\text{Sn}$ compounds from SnCl_2 and the appropriate sodium reagent failed. Other unsymmetrical stannocenes may be prepared according to Scheme 6.10 [90, 97, 155].

Stannocene forms a pale brown 1:1 and a brown 1:2 adduct with tetracyanoethylene and a pale lime-green 1:1 adduct with 7,7,8,8-tetracyanoquinodimethane, which are thermally quite stable and decompose only above 160°C . Their structures are unknown, but it is thought that they are charge transfer complexes involving the cyclopentadiene π -electron system [156].

A route to synthetically useful tin(II) compounds without Sn–C bonds is the cleavage of stannocenes (usually $(\text{MeC}_5\text{H}_4)_2\text{Sn}$) by protic species such as alcohols [157, 158], phenols [159], thiols [158], hydroxylamines [157], oximes [157], cyclic amines [157], carboxylic acids [157, 160], sulphonic acids [160], acetoacetals [161, 162] and the Schiff base *N,N'*-ethylenebis(acetylideneimine) [163]. These reactions usually proceed rapidly at room temperature in good yield to give products that are readily isolated. Such reactions have now been used to generate tin(II) species as intermediates for the organic synthesis of a variety of compounds such as optically active glycerol derivatives, esters, amides, *N*-alkyl imides, imides, and α,β -dihydroxyketones [164–168]. The enantioselective addition of Me_3SiCN to aldehydes can be effected by use of a chiral Sn(II) compound prepared from $(\text{MeH}_4\text{C}_5)_2\text{Sn}$, triflic acid and cinchonine [169]. Stannocene itself has also been found to react with Bu'SH to give $(\text{Bu'S})_2\text{Sn}$ in 65% yield [170].

Treatment of $(\text{Me}_5\text{C}_5)_2\text{Sn}$ with two equivalents of $\text{HC}_5(\text{CO}_2\text{Me})_5$ was originally thought to give the stannocene derivative $[(\text{MeO}_2\text{C})_5\text{C}_5]_2\text{Sn}$ [171] but X-ray crystallography has since shown that the product is in fact a covalent tin(II) product containing Sn–O bonds [151]. Ring substitution reactions of stannocenes can also be carried out without their displacement from the tin. A potentially very useful reaction has been the metallation of the cyclopentadienide rings by butyllithium to give a dilithium species which can subse-



Scheme 6.10

quently be derivatized using Me_3SiCl or $(\text{Pr}^i\text{N})_2\text{PCl}$ to give $[(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]_2\text{Sn}$ and $[(\text{Pr}^i\text{N})_2\text{PC}_5\text{H}_4]_2\text{Sn}$, respectively. Repeated metallation and derivatization of $(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Sn}$ leads to the formation of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sn}$ and $[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]_2\text{Sn}$ [96]. Other reactions in which ring substitutions occur are the oxidative addition of a C–H bond to the phosphonium salt $[(\text{Pr}^i\text{N})_2\text{P}]^+[\text{AlCl}_4]^-$ to give $\{(\text{MeC}_5\text{H}_4)[(\text{Pr}^i\text{N})_2\text{HPC}_5\text{H}_4]\text{Sn}\}^+[\text{AlCl}_4]^-$ [172] and the reaction of stannocene with $\text{Me}_3\text{SnNEt}_2$ to give a low yield of a mixed Sn(II)–Sn(IV) product, $(\text{Me}_3\text{SnC}_5\text{H}_4)_2\text{Sn}$ [173]. Stepwise nucleophilic substitutions of Cp_2Sn have also been shown to be possible. Treatment first with $\text{LiN}=\text{C}(\text{NMe}_2)_2$ leads to formation of the unusual centrosymmetric dimer *trans*- $\{[\text{Sn}(\eta^3\text{-C}_5\text{H}_5)[\mu\text{-N}=\text{C}(\text{NMe}_2)_2]]_2\}$; subsequent treatment with a lithiated dithiane $\text{Li}[\text{S}(\text{CH}_2)_3\text{SC}(\text{R})]$ ($\text{R} = \text{H}$ or SiMe_3) leads to the dimeric mixed-ligand species $\{[\text{Sn}[\text{S}(\text{CH}_2)_3\text{SC}(\text{R})][\mu\text{-N}=\text{C}(\text{NMe}_2)_2]]_2\}$ [174, 175].

The reaction between Cp_2Sn and Cp_2Mg in a 1:2 ratio leads to nucleophilic addition and the formation of $[\text{Mg}(\text{thf})_6]^{2+}2[\text{Sn}(\eta^3\text{-C}_5\text{H}_5)_3]^-$. The reaction between fluorenyl lithium and Cp_2Sn leads to nucleophilic substitution of both Cp ligands and the formation of $[\text{Li}(\text{thf})_4][\text{Sn}(\text{C}_{13}\text{H}_9)_3]^-$ in which the geometry at the tin is a distorted pyramid [176]. Treatment of Cp_2Sn with NaCp in the presence of PMEDTA leads to nucleophilic addition and the formation of the triorganostannate complex $[(\eta^5\text{-Cp})_2\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}^+\text{pmedta}]$ [177].

The antitumour activity of $(\text{Ph}_5\text{C}_5)_2\text{Sn}$ has been investigated. It was found to provoke cure rates of 40–90% in doses of 160–460 mg kg^{-1} but toxic deaths were caused by doses greater than 440 mg kg^{-1} . It is unclear, however, whether the activity is due to the tin atom or to the organic ligand [178]. The isopropenyl stannocene $(\text{CH}_2=\text{C}(\text{Me})\text{C}_5\text{H}_4)_2\text{Sn}$ does not undergo homopolymerization with SnCl_4 as initiator but does undergo free radical copolymerization with styrene initiated by AIBN [92].

The stannacarboranes $\text{Sn}(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4$, $\text{Sn}(\text{Me}_3\text{Si})(\text{Me})\text{C}_2\text{B}_4\text{H}_4$ and $\text{Sn}(\text{Me}_3\text{Si})\text{C}_2\text{B}_4\text{H}_5$ do not react with either BF_3 or $\text{BH}_3\cdot\text{THF}$ at room temperature [115], but do form donor–acceptor complexes with 2,2′-bipyridine with the tin atom acting as a Lewis acid [114, 140]. The tin atoms in these stannacarboranes can be displaced by treatment with half an equivalent of GeCl_4 in the absence of solvent at 150–160°C, giving SnCl_2 and the germanium(IV) sandwich compounds $\text{Ge}[2,3\text{-(Me}_3\text{Si)(R)-}2,3\text{-C}_2\text{B}_4\text{H}_4]_2$ ($\text{R} = \text{Me}_3\text{Si}$, Me or H) [116]. The dodecastannacarborane 2,3- Me_2 -1-Sn-2,3- $\text{C}_2\text{B}_5\text{H}_9$ is unreactive towards $\text{CF}_3\text{SO}_3\text{Me}$, MeI and SnCl_4 but it does form adducts with for example 2,2′-bipyridine, tetrahydrofuran and triphenylphosphine [117].

6.3.4 Transition metal complexes

The cyclopentadienyltin(II) derivatives form a variety of complexes with transition metals. Treatment of $(\text{C}_5\text{H}_5)_2\text{Sn}$ or $(\text{MeC}_5\text{H}_4)_2\text{Sn}$ with $\text{M}(\text{CO})_5\cdot\text{THF}$ complexes ($\text{M} = \text{Cr}$, Mo or W) gives rise to simple

donor-acceptor complexes $(C_5H_5)_2SnM(CO)_5$ ($M=Cr, Mo$ or W) and $(MeC_5H_4)_2SnM(CO)_5$ ($M=Cr$ or W) [175]. However, reaction of R_2Sn ($R=C_5H_5, MeC_5H_4$ or Me_5C_5) with $Fe_2(CO)_9$ gives a bridged dinuclear species $[(CO)_4FeSnR_2]_2$ in which the mode of attachment of the rings to tin has changed from penta- to monohapto. On dissolving these complexes in donor solvents, monomeric base-stabilized species $Fe(CO)_4SnR_2 \cdot 2B$ are formed (where $B=THF$ or pyridine) [179, 180]. Transition metal complexes containing the $CpSnX$ ($Cp=C_5H_5$ or C_5Me_5 , $X=Cl$ or Br) unit have been prepared similarly, for example the reaction between $Fe_2(CO)_9$ and two equivalents of C_5H_5SnX ($X=Cl$ or Br) gives the dimeric $[(CO)_4FeSn(C_5H_5)X]_2$ [180] and the reaction between $M(CO)_5SnCl_2(THF)$ ($M=Cr$ or W) and $Me_5C_5SnMe_3$ leads to loss of Me_3SnCl and the formation of $M(CO)_5SnCl(Me_5C_5)$ [160].

Transition metal hydrides can also react with stannocene with loss of both cyclopentadienyl rings from tin. Stannocene reacts with $HMn(CO)_5$ to give a ditin dihydride, $\{H[Mn(CO)_5]_2Sn\}_2$ [181] and with $HMo(CO)_3(C_5H_5)$ to give the tin hydride $HSn[Mo(CO)_3(C_5H_5)]_3$ [182]. The nature of the product formed in the reaction of 1,1'-dimethylstannocene with $HW(CO)_2(C_5H_5)$ has been the subject of several reports. The reaction was originally reported to yield the tin(IV) polymer $\{Sn[W(CO)_3C_5H_5]_2\}_n$ [157], but later the material was reformulated as an unusual transition metal derivative of tin(II), $Sn[W(CO)_3C_5H_5]_2$ [179]. The reaction is now thought to proceed like that of the molybdenum analogue to give initially the hydride $HSn[W(CO)_3C_5H_5]_3$, which can react further with a chlorinated solvent to give the chloride $ClSn[W(CO)_3C_5H_5]_3$ [183, 184].

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7 Tin-metal bonded compounds

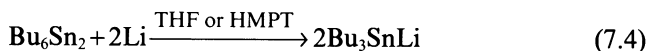
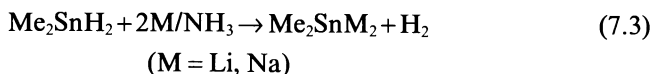
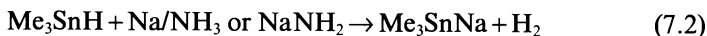
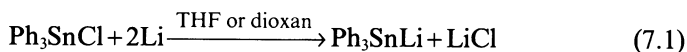
F. GLOCKLING

This chapter is devoted to the formation, structure, reactivity and physical properties of molecules containing one or more bonds between tin and another metal, including boron and silicon. Attention has been concentrated on work published since 1970. Reviews [1–12] include an account of applications to areas of chemistry including catalysis, hydrogenation and isomerization of alkenes and polymerization [11]. For comprehensive lists of compounds with organic groups bonded to tin, see ref 12.

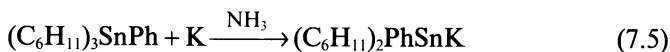
7.1 Tin-alkali metal compounds

Compounds of the type R_3SnM are known for all of the alkali metals M , and those of the type R_2SnM_2 for lithium and sodium. Although few structures have been reported, it is apparent from chemical behaviour, conductivity, Mössbauer and NMR studies that these compounds are essentially ionic with strong ion pairing [13, 14, 25].

The main preparative methods involve the cleavage of Sn-halide, Sn-H, Sn-C or Sn-Sn bonds by an alkali metal or an organo-derivative of an alkali metal. In general, these reactions proceed most satisfactorily in Lewis base solvents such as ether, THF, 1,2-dimethoxyethane (DME), liquid ammonia or HMPT, although it is as well to bear in mind that as strong nucleophiles they react slowly with some of these solvents. Illustrative examples are shown in eqns 7.1–7.4 [15–21].

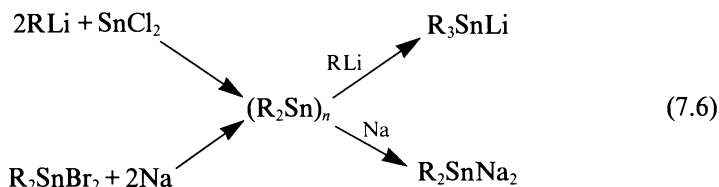


Bu_3SnM ($M = K, Cs$) have been obtained [22] from Bu_3SnH and $MNPr_2^i/LiOBu^i$. Selective cleavage of Sn-C bonds can result in unsymmetrical derivatives (eqn 7.5) [23].

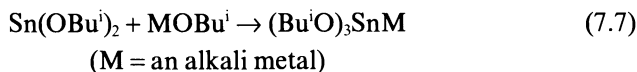


Stannane, SnH_4 , may be converted into either H_3SnNa or H_2SnNa_2 by the action of sodium in liquid ammonia [19, 24] and organohydrido tin anions $[\text{R}_n\text{SnH}_{3-n}]^-$ are similarly formed. Cleavage of Sn–C, Sn–Sn or Sn–halide bonds by sodium naphthalide in 1,2-dimethoxyethane may also be used to form R_3SnNa compounds [26].

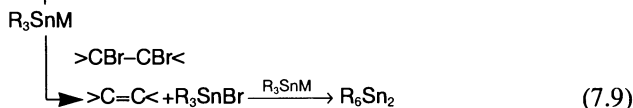
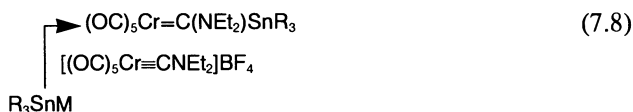
Cyclic or polymeric organotin compounds have been converted into R_3SnM or R_2SnM_2 by the types of reactions shown in eqn 7.6 [17, 26–29]:



In addition to organo-derivatives, Sn–O bonded analogues have been obtained [30] according to eqn 7.7:



Both R_3SnM and R_2SnM_2 compounds are strong nucleophiles and undergo a wide range of reactions analogous to those of organolithium and Grignard reagents. The utility of these compounds as synthetic reagents is discussed elsewhere (Chapter 9). Some of their less familiar reactions are given in eqns 7.8 and 7.9 [31, 32].

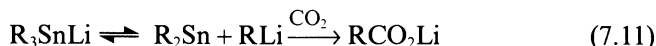


Irradiation of Ph_3SnM compounds in the presence of polycyclic aromatic hydrocarbons gives the radical anion of the hydrocarbon [33]. R_3SnLi compounds decompose rapidly with first order kinetics in THF in the presence of Sn_2R_6 , giving mainly SnR_4 , together with $\text{Sn}_2\text{R}_5\text{Li}$, elemental tin and polymeric material [34, 35].

Although halogen–metal exchange and subsequent coupling reactions are frequently observed in reactions with organic or metal halides, there are many examples, such as eqn 7.10 [36], in which the nucleophilic substitution product is formed in quite high yield:



Until recently, little information on the structure of these compounds has been available. The crystal structure of $\text{Li}[\text{Sn}(\text{2-furyl})_3]$, as a dioxan solvate, reveals the ionic structure $[\text{Li}(\text{dioxane})_4]^+[\text{Sn}(\text{2-furyl})_3\text{Li}(\text{2-furyl})_3\text{Sn}]^-$ in which lithium appears in both the anion and cation. In solution R_3SnM compounds ($\text{R} = \text{Et}, \text{Bu}$) appear, on the basis of their reaction with CO_2 to be in equilibrium with RLi [26] (eqn 7.11).



When $\text{R} = \text{Ph}$, this equilibrium is said to be well to the left, and on reaction with CO_2 it yields Ph_6Sn_2 and oxalate, consistent with a charge transfer reaction and subsequent coupling of the resulting radicals. Similarly, oxidation of Ph_3SnNa with O_2 gives the products of radical coupling (Ph_6Sn_2 and Na_2O_2) [26]. R_3SnM compounds form charge transfer complexes with electron acceptors like 1,3,5-trinitrobenzene [37]. Solutions of SnMe_4 and MeLi in THF/HMPA form an *ate* complex, $\text{Li}[\text{SnMe}_5]$, probably with a trigonal bipyramidal arrangement of methyl groups about tin [38].

Ph_3SnK , formed from Ph_3SnCl and K/NH_3 , is a yellow crystalline solid and in the crown ether derivative $\text{K}[18\text{-crown-6}][\text{Ph}_3\text{Sn}]$, $[\text{Ph}_3\text{Sn}]^-$ is pyramidal with an average $\text{Sn}-\text{C}$ distance 10 pm longer than in Ph_4Sn [25]. The related monomeric complex, $\text{Ph}_3\text{SnLi}(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$ contains a direct $\text{Sn}-\text{Li}$ bond, both Sn and Li being four-coordinate. Its ^7Li NMR shows coupling to ^{117}Sn and ^{119}Sn [39]. A highly interesting crystalline complex (eqn 7.12) has been characterized in which the alkali metal is free from O- or N-coordinated ligands.

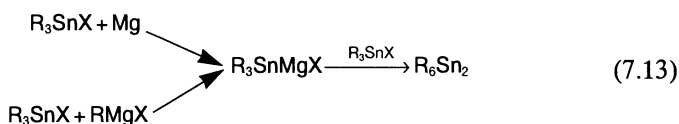


In this complex the neopentyl groups are pyramidal about tin with an average $\text{C}-\text{Sn}-\text{C}$ angle of 91.7° , indicating little *s*-character to the $\text{Sn}-\text{C}$ bonds [40].

7.2 Tin-Group 2 metal compounds

No attempts have apparently been made to form tin-beryllium compounds, even though their structures would be of considerable interest in relation to corresponding lithium and Grignard derivatives. Nor is there any report of tin compounds with strontium or barium.

In the reaction between Grignard reagents and SiCl_4 or GeCl_4 appreciable yields of R_6M_2 products result, especially in the presence of free finely divided magnesium or with sterically demanding R groups. Similar observations have been made for the analogous reaction of tin tetrahalides, and these can be rationalized in terms of the formation of an intermediate magnesium halide derivative, R_3SnMgX (eqn 7.13) [41, 42].



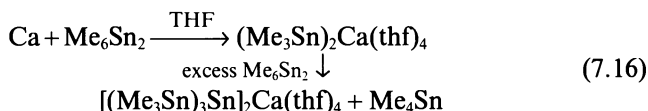
Similarly, sterically hindered Grignard reagents react with Bu_3SnH with the formation of Bu_3SnMgCl [43] (eqn 7.14):



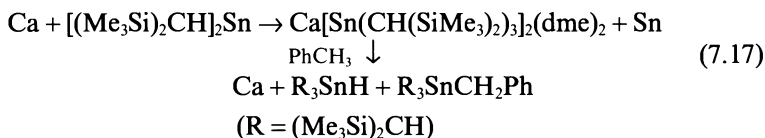
Ph_3SnH and $\text{EtMgBr}(\text{NEt}_3)$ in ether at -15°C yield an oil formulated as $\text{Ph}_3\text{SnMgBr} \cdot \text{NEt}_3$ which loses Et_3N *in vacuo* giving the dimer $(\text{Ph}_3\text{SnMgBr})_2$ [44]. Further evidence for R_3SnMgX derivatives comes from the reaction between Ph_3SnCl or Ph_6Sn_2 and magnesium in THF containing a small amount of ethyl bromide since, on hydrolysis, Ph_3SnH is formed [45]. As with R_3SnLi compounds there is some evidence for dissociation in solution (eqn 7.15) [46].



Calcium and Me_6Sn_2 react in THF to form a Ca–Sn bonded complex [46] in which Ca is six-coordinated, the C–Sn–C bond angle of 96.5° being indicative of high *p*-character of the Sn–C bonds (eqn 7.16).



With bulky bis(trimethylsilylmethyl) groups bonded to tin, a reactive four-coordinated Ca complex is formed in DME which decomposes in toluene solution [47] (eqn 7.17).



7.3 Scandium, yttrium, lanthanides and actinides

The Sc–Sn(II) complex $(\text{C}_5\text{H}_5)_2(\text{Me})\text{Sc-Sn}[\text{N}(\text{SiMe}_3)_2]$, has been obtained [48] as a pale yellow oil by reacting $(\text{C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Me}_2)\text{AlMe}_2$ with $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$. Three types of lanthanide–tin bonded compounds have been described. Reaction between MCl_3 and Ph_3SnLi in THF at -80°C has so far yielded $\text{M}(\text{SnPh}_3)_3$ for $\text{M} = \text{Pr}$, Nd , Gd and Er , which with excess Ph_3SnLi are converted into the complex anions $\text{Li}(\text{thf})_n[\text{M}(\text{SnPh}_3)_4]$. Reaction between Ph_3SnLi and $(\text{C}_5\text{H}_5)_2\text{MCl}$ ($\text{M} = \text{Er}$ or Yb) gives the coloured complexes

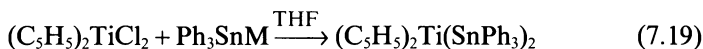
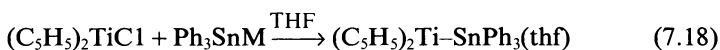
$(C_5H_5)_2MSnPh_3$. Thermal decomposition of the complexes is observed above $200^\circ C$ [49]. The lanthanides praseodymium, neodymium, holmium and lutetium react with $Hg[Sn(C_6F_5)_3]_2$ to give air- and water-sensitive products of the type $(C_6F_5)_3SnMHgSn(C_6F_5)_3$ [50], like the germanium analogues [51]. Reaction of $(Me_3SiCH_2)_3SnH$ with $M[N(SiMe_3)_2]_3$ in DME yields, for praseodymium and neodymium, the complexes $(R_3Sn)_3M(dme)$. Reaction with $(PhCOO)_2$ leaves one Sn–Ln bond intact, forming $R_3Sn-Ln(OCOPh)_2$. Similar reactions with Et_3SnH and praseodymium or neodymium are more complex due to cleavage of a methyl group from the solvent. In these cases the products have been formulated as $Et_3SnM(OCH_2CH_2OMe)_2$ [52].

Ph_4Sn and $C_{10}H_8Yb(thf)_2$ form two products: $(Ph_3Sn)_2Yb(thf)_4$ and $Ph_3Sn-Yb(thf)_3(\mu_2-Ph_3)Yb(thf)_3$. Bromine cleaves the Sn–Yb bond in the latter compound forming Ph_nSnBr_{4-n} , $PhBr$ and $YbBr_3$ [30].

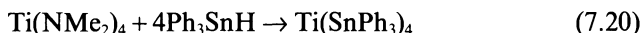
The only U–Sn complex so far described has been obtained by the room temperature reaction of $(C_5H_5)_3UX$ ($X=CH_3, NEt_2$) in toluene with Ph_3SnH , forming $(C_5H_5)_3U-SnPh_3$ as a bright green solid. It decomposes at $60-70^\circ C$, is unstable in Lewis base solvents and is readily oxidized and hydrolysed. The structure consists of two distorted tetrahedra about the two metal atoms. Unexpectedly, Bu_3SnH apparently does not undergo this reaction [50, 53].

7.4 Titanium, zirconium and hafnium

All three metals are known to form tin complexes in their zero, +2, +3 and +4 oxidation states. Ti(III)- and Ti(IV)-tin compounds have been obtained by classical nucleophilic displacement reactions (eqns 7.18 and 7.19):



With an excess of Ph_3SnK in monoglyme, the anion $[(C_5H_5)_2Ti(SnPh_3)_2]^-$ is obtained [54, 55]. Titanium(IV) and zirconium(IV) complexes have also been formed from the amide and tin hydride by hydrostannolysis [56] (eqn 7.20).

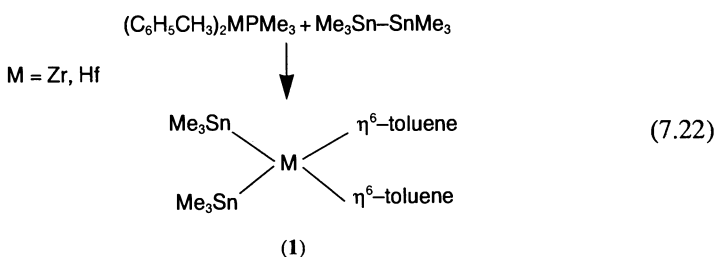


In the presence of added methanol, this reaction can yield $Ti(SnPh_3)_2(OMe)_2$. The dark green paramagnetic Ti(III)–Sn complex $(C_5H_5)_2Ti-SnPh_3(thf)$ is oxidized in $CHCl_3$ solution to $(C_5H_5)_2(Cl)Ti-SnPh_3$, a diamagnetic green solid [54]. For all three metals this type of compound can be made directly from the M(IV) complex (eqn 7.21) [57].



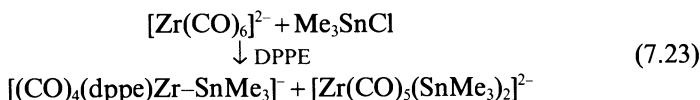
These chloro complexes are coloured yellow or orange and are thermally stable solids. The M–Sn bond is cleaved by hydrogen halides to give Ph_3SnH and $(\text{C}_5\text{H}_5)_2\text{MX}_2$, consistent with bond polarity in the sense $\text{M}\delta^+ - \text{Sn}\delta^-$ [58]. Highly reactive bis(naphthalene)titanium and $\text{Me}_3\text{SnK}(15\text{-crown-5})$ yield the 16-electron complex $[\text{K}(15\text{-crown-5})]_2[(\text{Me}_3\text{Sn})_2\text{Ti}(\eta^4\text{-C}_{10}\text{H}_8)_2]$ with an average Sn–Ti distance of 286.6 pm [59].

The Zr and Hf complexes $\text{Ph}_3\text{Sn-M}(\text{C}_5\text{H}_5)_2\text{Cl}$ have been isolated as coloured crystalline solids by standard nucleophilic substitution reactions [60], and both the zirconium and hafnium complexes (1) have been obtained by an oxidative addition reaction (eqn 7.22) [61].



The hafnium complex (1) forms black crystals decomposing in air over several hours and is very rapidly oxidized in solution. The Sn–Hf–Sn bond angle is $< 90^\circ$ [61].

Hydrostannolysis of $\text{Ti}(\text{NMe}_2)_3$ or $[(\text{C}_5\text{H}_5)_2\text{TiNMe}_2]_2$ using Ph_3SnH results in the formation of titanium(III) compounds, believed to be $\text{Ti}(\text{SnPh}_3)_3$ and $(\text{C}_5\text{H}_5)_2\text{Ti-SnPh}_3$, respectively [62]. The far less thermally stable triethyltin complexes $(\text{C}_5\text{H}_5)_2\text{M-SnEt}_3$ ($\text{M} = \text{Ti, Zr}$) have been formed from $(\text{C}_5\text{H}_5)_2\text{M}$ and Et_3SnLi in THF or toluene at -40°C ; decomposition occurs at -20°C to Sn_2Et_6 [63]. Highly unstable Zr(0) complexes have been isolated and characterized [64] (eqn 7.23):

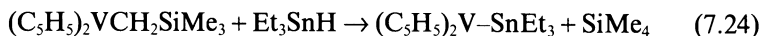


A crystalline Zr(II)–Sn(II) complex, $(\text{C}_5\text{H}_4\text{CH}_3)_2\text{Zr}(\text{SnR}_2)_2$, [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH-}$] is formed from $(\text{C}_5\text{H}_4\text{CH}_3)_2\text{ZrBu}_2$ and SnR_2 . It has pseudo-tetrahedral geometry at Zr with two equivalent Zr–Sn bonds; calculations suggest that there is significant π -interaction between Zr and Sn [65].

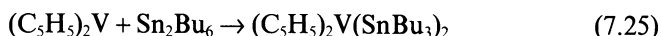
7.5 Vanadium, niobium and tantalum

All of these metals form bonds to tin, with a similar chemistry for each metal. The formal oxidation states involved are -1 , $+1$, $+3$, $+4$ and $+5$. The high

reactivity of the Sn–H bond has been used in forming V–Sn compounds (eqn 7.24) [66].



$(\text{C}_5\text{H}_5)_2\text{V-SnEt}_3$ is a dark blue solid, stable at room temperature but very readily oxidized by air. It reacts with 1,2-dibromoethane forming ethene, Et_3SnBr and $(\text{C}_5\text{H}_5)_2\text{VBr}_2$ [66]. The V–Sn bond is also cleaved by acids, alcohols and Na or Na/Hg [10, 67]; thermal decomposition gives primarily $(\text{C}_5\text{H}_5)_2\text{V}$ and Sn_2Et_6 . The reverse type of reaction appears to take place with Sn_2Bu_6 in THF (eqn 7.25) [68].

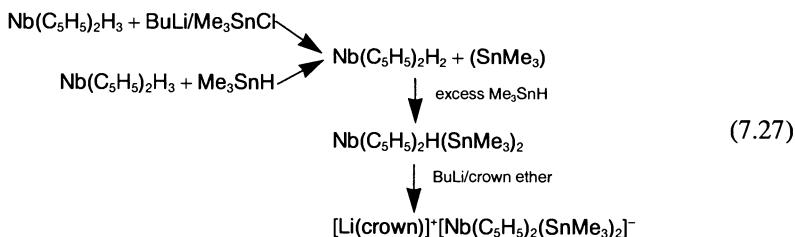


However, this V(IV) product has not been isolated. A further preparative method makes use of the high reactivity of Sn–N bonds [69] (eqn 7.26); $\text{Me}_n\text{SnCl}_{4-n}$ compounds show similar reactivity towards tantalum hydrides [70].

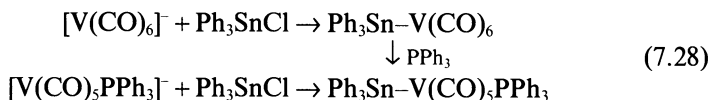


Mössbauer, IR and NMR spectroscopy reveal that compounds of this type have a symmetrical structure with two terminal Ta–H and a central Ta–Sn bond, a structure which has been confirmed by X-ray analysis in the case of $(\text{C}_5\text{H}_5)_2(\text{H})_2\text{Ta-SnMe}_2\text{Cl}$. Other +3 oxidation state complexes which have been examined crystallographically include $\text{Ph}_3\text{Sn-Nb}(\text{CO})(\text{C}_5\text{H}_5)_2$ and its SnCl_3 analogue [71].

Aspects of Nb–Sn chemistry are illustrated in (eqn 7.27) [72].

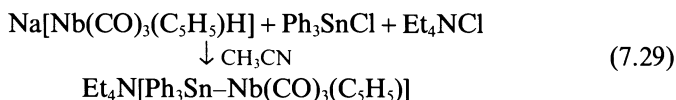


Seven-coordinated V(I)–Sn(IV) complexes have been obtained from the 18-electron six-coordinated hexacarbonyl vanadium anion (eqn 7.28):



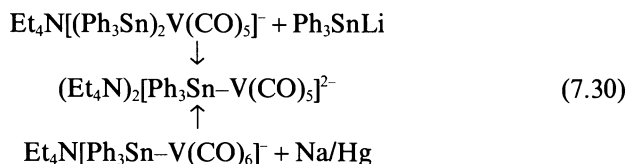
These coloured complexes are of low thermal stability and readily oxidized [73]. Other compounds of vanadium, niobium and tantalum in their +1 oxidation state include $\text{Ph}_3\text{Sn-M}(\text{CO})_5\text{P(OPh)}_3$ and $\text{Ph}_3\text{Sn-M}(\text{CO})_4[\text{PPh}_2\text{CH}_2]_2$ [74].

Anionic complexes have been obtained from reactions of the type (eqn 7.29):

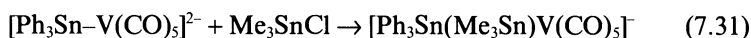


In this complex, tin is in a highly distorted tetrahedral environment, the overall geometry at niobium being that of a four-legged 'piano stool' [75, 76]. Another seven coordinate ion $[(\text{Ph}_3\text{Sn})_2\text{V}(\text{CO})_5]^-$ (formed from $[(\text{CO})_5\text{V}-\text{SnPh}_3]^{2-}$ and Ph_3SnCl), does not have the expected pentagonal bipyramidal structure. Various descriptions of the geometry are possible: monocapped trigonal prism, trigonal base-tetragonal base or a monocapped octahedron [77].

Doubly charged 18-electron anionic complexes have been made by two routes (eqn 7.30) [77].



This reaction has also been applied to the synthesis of phosphine substituted derivatives. Reaction of the $[(\text{Ph}_3\text{Sn})_2\text{V}(\text{CO})_5]^-$ ion with ethanoic acid in THF gives what is possibly the hydride $[\text{Ph}_3\text{Sn}-\text{V}(\text{H})(\text{CO})_5]^-$ as an unstable orange-red complex. Mixed organotin anions have been obtained by the reaction (eqn 7.31):

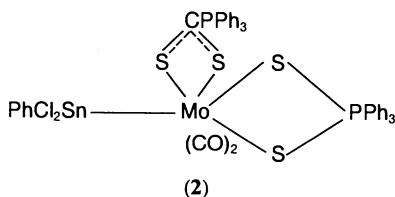


Trichlorotin complexes may be made by similar reactions (eqn 7.32) [78].

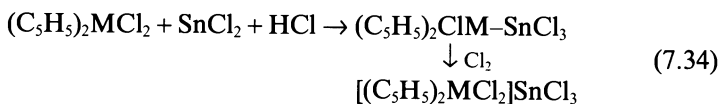
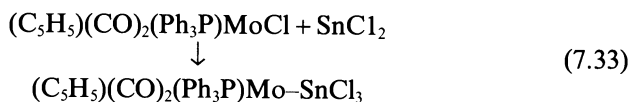


7.6 Chromium, molybdenum and tungsten

All three metals form $\text{Sn}-\text{M}$ complexes with M in oxidation states of -1 , zero and $+2$ as neutral and anionic complexes, and with tin in its $+2$ and $+4$ oxidation states. Coordination numbers of 2, 4, 5 and 6 are encountered for tin, and with one exception Lewis-base ligands are bonded to the transition metal. Interesting structures have been found: many $\text{Mo}-\text{Sn}$ complexes are seven-coordinated about Mo , e.g. (2) which has a distorted capped octahedral geometry [79]. The reaction of $\text{Cr}(\text{CO})_3(\text{mesitylene})$ with K_4Sn_9 in the presence of a cryptate gives the complex $(\text{K-crypt})_4[\text{Sn}_9\text{Cr}(\text{CO})_3]^{4-}$ as a bicapped square anti-prismatic cluster, isoelectronic with $[\text{B}_{10}\text{H}_{10}]^{2-}$ [80].

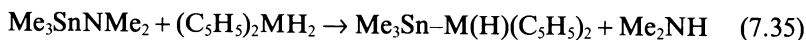


The reaction of SnX_2 with $\text{M}-\text{M}$ bonded complexes of the type $[\text{M}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ produces two products according to the experimental conditions: $\text{X}_2\text{Sn}[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ and $\text{X}_3\text{Sn}-\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3$ [81]. Insertion of SnX_2 into $\text{M}-\text{X}$ bonds has also been extensively used. Subsequent oxidation by halogen cleaves the $\text{M}-\text{Sn}$ bond (eqns 7.33 and 7.34) [82].

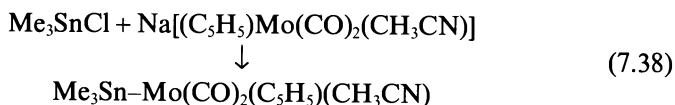
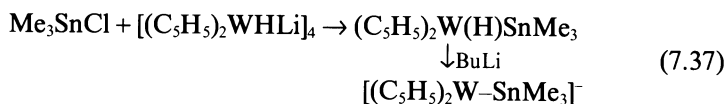
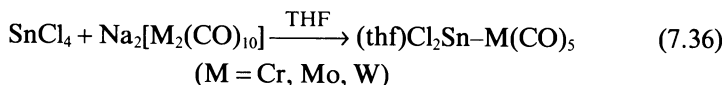


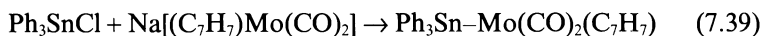
The crystal structure of $\text{Br}_3\text{Sn}-\text{Mo}(\text{C}_5\text{H}_5)_2\text{Br}$ confirms the presence of the $\text{Sn}-\text{Mo}$ bond [83].

Treatment of SnCl_2 with $\text{K}_2[\text{Cr}(\text{CO})_5]$ in the presence of [2.2.2] cryptand yields a remarkable anionic cluster $\{[(\text{CO})_5\text{Cr}]_6\text{Sn}_6\}^{2-}$ with an octahedron of tin atoms, each bonded to a $-\text{Cr}(\text{CO})_5$ group [84]. On exposure to $\text{O}_2/\text{H}_2\text{O}$, the anion $\{\text{Cl}_2\text{Sn}[\text{Cr}(\text{CO})_5]_2\}^{2-}$ is converted into a rhombododecahedral complex, $[(\text{CO})_5\text{Cr}-\text{Sn}]_6(\mu_3-\text{O})_4(\mu_3-\text{OH})_4$ in which O and OH bridge adjacent Sn atoms [85]. A versatile method of forming $\text{Sn}-\text{M}$ bonds for these metals is the reaction between an organotin amide and a metal hydride complex (eqn 7.35). The order of reactivity is $\text{CrH} > \text{MoH} > \text{WH}$ for related complexes [69].

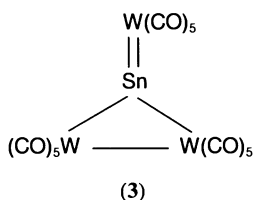


Anionic transition metal complexes may also be used in synthesis (eqns 7.36–7.41) [86–91].

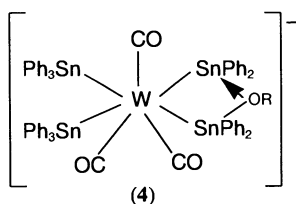




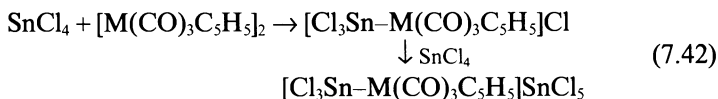
Reaction of $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$ with SnCl_4 gives the planar metal cluster complex (3) in which the W–Sn ring bond lengths are 278 pm, the exo W–Sn length being significantly shorter at 270 pm [92].



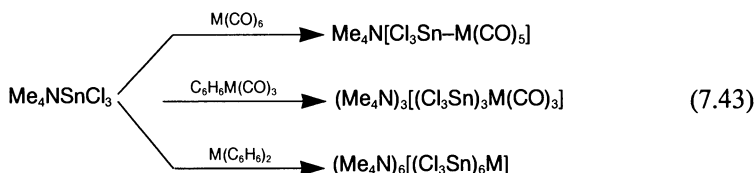
Reduction of complexes of the type $\text{W}(\text{CO})_3\text{L}_3$ ($\text{L} = 1,1,4,7,7$ -pentamethyldiethylenetriamine) with K/NH_3 gives tungsten carbonyl anions of unknown structure which react with Ph_3SnCl in ethanol to give seven-coordinated complexes such as $(\text{Me}_4\text{N})_2[\text{HW}(\text{CO})_3(\text{SnPh}_3)_3]$ or $\text{Ph}_4\text{P}[(\text{Ph}_3\text{Sn})_2\{(\text{Ph}_2\text{Sn})_2\text{OEt}\}\text{W}(\text{CO})_3]$. In the latter compound, the $(\text{Ph}_2\text{Sn})_2\text{OEt}$ unit functions as a bidentate ligand as in (4) [93, 94].



When SnCl_4 reacts with neutral molybdenum or tungsten complexes, cationic products with an $\text{M}-\text{SnCl}_3$ bond are formed (eqn 7.42).

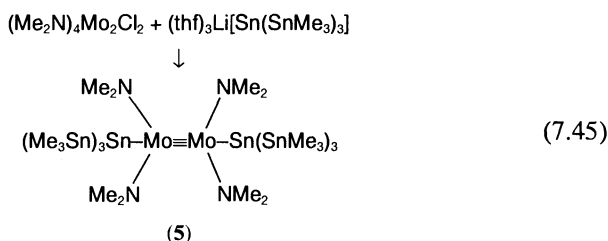


$\text{Sn}-\text{M}$ bonds ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) may be formed using anionic tin species (eqns 7.43 and 7.44) [78].

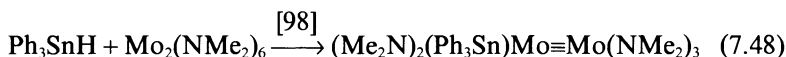
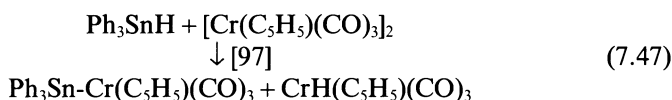
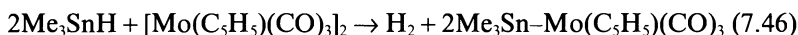




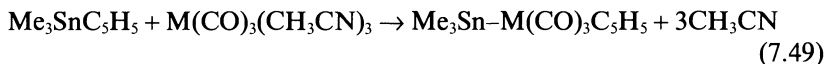
Some of these anionic complexes are stable to air and water [89]. The complex $\text{Et}_4\text{N}[(\text{Ph}_3\text{Sn})_3\text{Cr}(\text{CO})_4]$, in which chromium is seven-coordinated with approximately C_{3v} symmetry, reacts with Ph_3SnLi in HMPA forming the six-coordinated anion $[(\text{Ph}_3\text{Sn})_2\text{Cr}(\text{CO})_4]^{2-}$ [95]. Starting from an Mo(III) compound with a Mo–Mo triple bond, this type of reaction has yielded the triply bonded Mo≡Mo complex (5), with a Mo–Mo bond length of 220.1 pm [96].



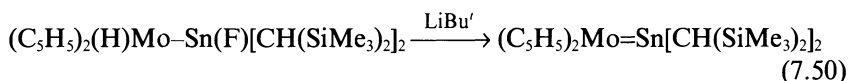
Oxidative addition of organotin hydrides to chromium, molybdenum and tungsten complexes represents a further method of establishing the tin–metal bond (eqns 7.46–7.48).



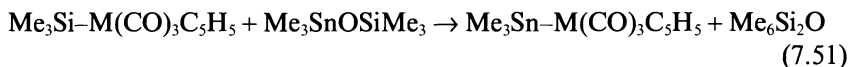
Closely related is the oxidative addition of cyclopentadienyltin compounds to the transition metal ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (eqn 7.49) [99].



A very novel Sn–Mo complex, tentatively formulated as $(\text{C}_5\text{H}_5)_2\text{Mo}=\text{SnR}_2$, has been isolated from reaction 7.50 [100].

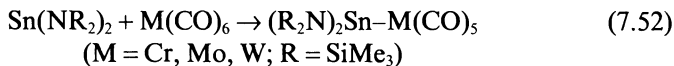


The greater reactivity of M–Si or M–Ge bonds can be used in synthesis (eqn 7.51) [101].

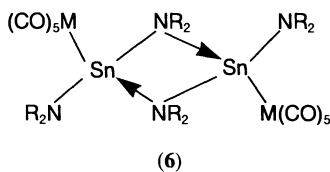


Cleavage of the W-CH₃ bond in C₃H₅(CH₃)W(CO)₃ by SnCl₂ gives (C₃H₅)(CO)₃W-SnCl₃ [102].

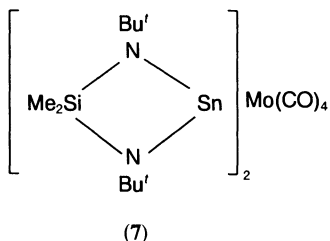
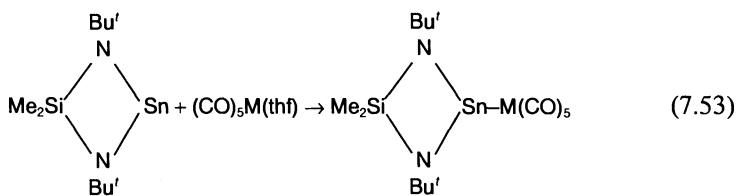
Reactions of stable stannylenes with transition metal complexes can take a variety of forms: they can behave as neutral Lewis-base donors displacing, for example, CO (eqn 7.52) [48].



With substituted metal carbonyls, M(CO)₄L₂, *trans*-disubstituted derivatives can be isolated, [(R₂N)₂Sn]₂M(CO)₄. Reaction of Sn(NR₂)₂ with M(CO)₅(thf) (M = Cr, Mo, W) gives the dimer [(R₂N)₂Sn-M(CO)₅]₂ (6) with a four-membered SnNSnN ring. In THF this complex breaks down to the monomer (R₂N)₂(thf)Sn-M(CO)₅ [103].

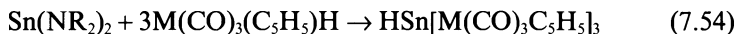


Irradiation of M(CO)₆ (M = Cr, Mo, W) and Sn[N(SiMe₃)₂]₂ in hexane gives both mono- and disubstitution products [104, 105], the stereochemistry about tin being trigonal planar [105]. Similarly, using M(CO)₄ (norbornadiene) gives exclusively *trans*-(R₂Sn)₂M(CO)₄ [106]. However, with less bulky ligands the tin becomes tetrahedrally coordinated by incorporation of a solvent molecule, e.g. in (thf)Bu'₂Sn-Cr(CO)₅. The pyridine analogue has an Sn-Cr bond length of 265.4 pm with distorted tetrahedral geometry about tin [105, 107, 108]. This is also the case for the product of reaction 7.53 [109].

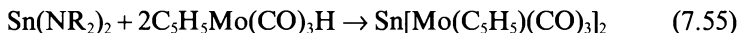


The similar molybdenum complex (7) has also been prepared [110].

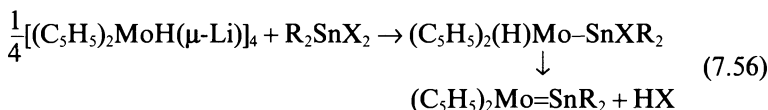
Reaction of $\text{Sn}(\text{NR}_2)_2$ with hydride complexes of Mo and W has given $\text{Sn}(\text{IV})$ products by oxidative addition (eqn 7.54) [111].



A similar reaction leads to the formation of the dark red two-coordinated $\text{Sn}(\text{II})$ complex (eqn 7.55) [48].



It is also possible to convert an $\text{M-Sn}(\text{IV})$ complex into an $\text{M-Sn}(\text{II})$ complex as in eqn 7.56 [112].



The photochemical reaction between $\text{W}(\text{CO})_6$ and SnCl_4 gives $(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3$ and, with Lewis bases, this complex yields two seven-coordinated complexes e.g. $\text{WCl}_2(\text{CO})_3(\text{PPh}_3)_2$ and $\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2$ [110].

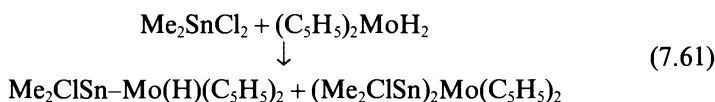
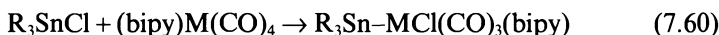
Bis(cyclopentadienyl)tin reacts with $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ in the same way as the tin(II) amide to give $\text{HSn}[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_3$. This reaction seems to proceed via $\text{Sn}[\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]_2$, which then reacts oxidatively with $\text{HMo}(\text{CO})_3\text{C}_5\text{H}_5$ [113]. In its photochemically induced reaction with $\text{Cr}(\text{CO})_6$, $\text{Sn}(\text{C}_5\text{H}_5)_2$ behaves as a two-electron donor giving $(\text{C}_5\text{H}_5)_2\text{Sn-Cr}(\text{CO})_5$ [69].

In $\text{Et}_4\text{N}[\text{Me}_3\text{Sn-W}(\text{PhC}\equiv\text{CPh})_3]$, formed from $[\text{W}(\text{PhC}\equiv\text{CPh})_3\text{CO}]^-$, $\text{LiC}_{10}\text{H}_8$ and Me_3SnCl followed by Et_4NCl , NMR data suggests a high $5s$ character to the Sn-W bond and a high p -character to the Sn-C bonds, suggesting its formulation as $\{[\text{W}(\text{PhC}\equiv\text{CPh})_3]^0(\text{Me}_3\text{Sn})\}^-$ [111].

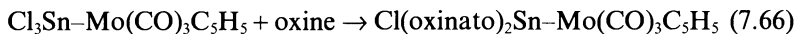
Bis[bis(trimethylsilyl)methyl]tin, R_2Sn , reacts oxidatively with chromium and molybdenum hydrides and alkyls [91] (eqns 7.57 and 7.58):



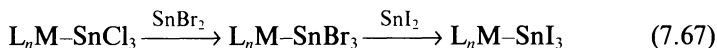
Methylation of $(\text{Me}_3\text{Si})_2\text{CH}(\text{Cl})_2\text{Sn-W}(\text{C}_5\text{H}_5)_2\text{H}$ by methyl lithium proceeds without cleavage of the Sn-W bond to give $(\text{Me}_3\text{Si})_2\text{CH}(\text{Cl})\text{MeSn-W}(\text{C}_5\text{H}_5)_2\text{H}$ [114]. Other oxidative addition reactions employ Sn-Sn and Sn-Cl bonded compounds [99, 115–117] (eqns 7.59–7.61).



Substitution of anionic ligands on tin proceeds without Sn-M bond breaking, and in the case of 8-hydroxyquinoline (eqn 7.66) the product is six-coordinate about tin [121].

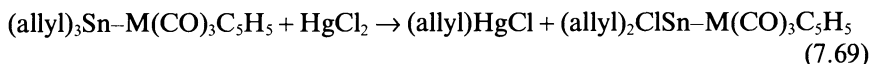


Similarly, halide exchange occurs readily at tin [122]:



Compounds described as $\text{R}_2\text{Sn}[\text{Cr(CO)}_3(\text{arene})]_2$ ($\text{R} = \text{Me}, \text{Ph}$) can be oxidized electrochemically to stable cations. However, the formulation of these compounds must be incorrect, and they probably contain R_2Sn groups bonded to the arene ligand [123]. Methyl lithium reacts with a CO ligand of $\text{Ph}_3\text{Sn-M(CO)}_3\text{C}_5\text{H}_5$ forming a carbene without cleaving the Sn-Mo bond [124]. The complexes $\text{Ph}_3\text{Sn-M(CO)}_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) react with liquid sulphur dioxide at 25 °C, mainly by Sn-C bond cleavage to give di-insertion products. By contrast, the chromium compound is unreactive, as are the complexes $\text{Ph}_2\text{Sn[M(CO)}_3\text{C}_5\text{H}_5]_2$ ($\text{M} = \text{Mo}, \text{W}$) [125].

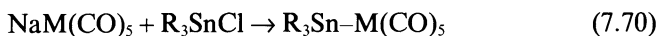
Reaction of the $[\text{Ph}_3\text{Sn-W(CO)}_5]^-$ anion with HCl results in cleavage of the Sn-Ph bond [126] whereas reactions with halogens and ICl cleave the Sn-M bond. The kinetics suggest that the reactions proceed via an intermediate in a two-step process [127-130]. RHgCl and HgCl_2 also cleave the Sn-M bond, though not in all cases (eqns 7.68, 7.69) [131]:

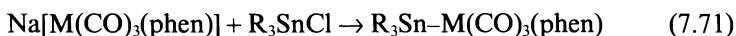


Photolysis of $\text{Me}_2\text{Sn[Mo(CO)}_3\text{C}_5\text{H}_5]_2$ or $\text{Me}_2\text{ClSn-Mo(CO)}_3\text{C}_5\text{H}_5$ gives $\text{Mo}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2$ [132].

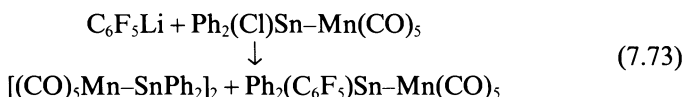
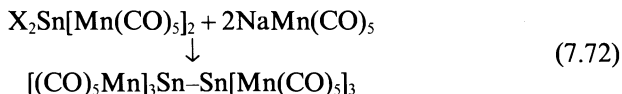
7.7 Manganese, technetium and rhenium

No technetium-tin bonded compounds have been described. For manganese, all examples involve the metal in its +1 or +2 oxidation state combined either to Sn(II) or Sn(IV). For rhenium, both the +1 and +3 oxidation states have yielded tin complexes. Neutral and cationic complexes feature in the chemistry. In most cases the transition metal has Lewis base donors (CO, R_3P) bonded to it, and these complexes are generally of high thermal and oxidative stability. Manganese and rhenium form a wide range of readily prepared anionic complexes (eqns 7.70 and 7.71) and these are commonly used in synthesis [133-135].



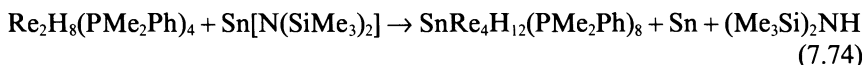


With tin halides possessing more than one Sn–Cl bond, further substitution can occur, and with SnCl_4 , three chlorines may be replaced giving $\text{ClSn}[\text{Mn}(\text{CO})_5]_3$ [133]. Complications can occur due to halogen–metal exchange and subsequent coupling reactions [133], e.g. eqns 7.72 and 7.73.

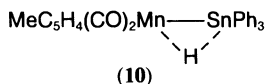


The dimeric structure of $[(\text{CO})_5\text{Mn}-\text{SnPh}_2]_2$ is based on a four-membered $\text{Mn}-\text{Sn}-\text{Mn}-\text{Sn}$ ring. In $\text{XSn}[\text{Mn}(\text{CO})_4(\text{PPh}_3)]_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), the Ph_3P ligand is *trans* to tin for all three halogens [136, 137]. The crystal structure of $\text{Br}_2\text{Sn}[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ has also been reported [138].

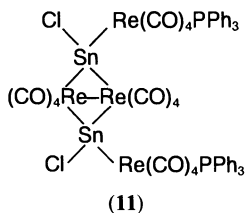
The product of the $\text{Sn}(\text{II})$ amide reaction (eqn 7.74) is remarkable: it consists of two $\text{P}_2\text{Re}-\text{ReP}_2$ units forming an elongated tetrahedron about the central four-coordinated tin atom. In this complex Sn–Re distances range from 262.7 to 279.3 pm [139].



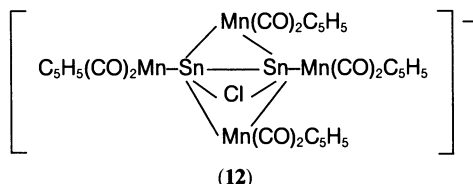
Whereas Ph_3SnH and $\text{C}_5\text{H}_5\text{Re}(\text{CO})_3$ yield H_2 , CO and $\text{C}_5\text{H}_5\text{Re}(\text{CO})_2(\text{SnPh}_3)_2$, the photochemical reaction between Ph_3SnH and $\text{MeC}_5\text{H}_4\text{Mn}(\text{CO})_3$ gives (10). NMR and crystallographic data show that in this complex hydrogen bridges Sn and Mn, akin to an agostic C–H bond [140].



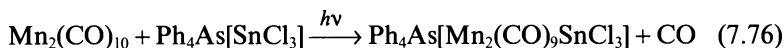
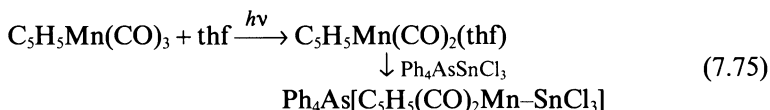
The reaction between SnX_2 and $\text{M}_2(\text{CO})_8(\text{PPh}_3)_2$ gives two types of product: $\text{ClSn}[\text{M}(\text{CO})_4\text{PPh}_3]_3$ and $\text{M}_2(\text{CO})_8[\mu-\text{Sn}(\text{Cl})\text{M}(\text{CO})_4\text{PPh}_3]_2$. The structure of the latter compound ($\text{M}=\text{Re}$) (11) consists of a planar $[\text{Re}_2\text{Sn}_2]$ rhombus with a *trans*-annular Re–Re bond; each tin(IV) atom is also bonded to a chlorine and $\text{Re}(\text{CO})_4(\text{PPh}_3)$ [141].



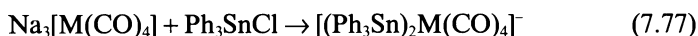
The anion $[\text{C}_5\text{H}_5(\text{CO})_2\text{MnHMn}(\text{CO})_2\text{C}_5\text{H}_5]^-$ and SnCl_2 combine to form the complex anion (12) in which Cl and two manganese atoms bridge the Sn-Sn unit. In this complex tin may be considered to be in its zero oxidation state or as a $(\text{Sn}_2)^{2-}$ unit [142].



Reaction of SnX_2 ($\text{X} = \text{Br}, \text{I}$) and $\text{Mn}_2(\text{CO})_{10}$ gives the metal cluster complexes $\text{X}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $\text{Mn}_2(\text{CO})_8[1,1-\mu\text{-Sn}(\text{X})\text{Mn}(\text{CO})_5]_2$ [143]. Photochemical methods have been successful in forming M-Sn bonds (eqns 7.75 and 7.76) [144].



In the latter reaction no disubstitution is observed. Reduction of $[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Mn}$ or Re) by sodium in HMPT gives the metal in its lowest oxidation state, and subsequent reaction with organotin halides results in the formation of anionic complexes [145]:



The reaction of the amidostannylenes $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ with $\text{BrMn}(\text{CO})_5$ at 20°C results in oxidation of the tin and formation of an Sn-Mn bond giving $\text{Br}(\text{R}_2\text{N})_2\text{Sn-Mn}(\text{CO})_5$ [48]. When the transition metal has more than one neutral ligand bonded to it, isomers of the resulting octahedral complex are usually isolated, as in the reaction between Me_3SnBr and $\text{Na}[\text{Mn}(\text{CO})_5(\text{PPh}_3)_2]$. Isomer interchange in the resulting complex, $\text{Me}_3\text{Sn-Mn}(\text{CO})_5(\text{PPh}_3)_2$, proceeds by an intramolecular process. This reaction also yields $\text{Me}_2\text{BrSn-Mn}(\text{CO})_3(\text{PPh}_3)$ by a redistribution process [146, 147]. Other unpredictable reactions include that between $\text{Sn}(\text{C}_5\text{H}_5)_2$ and $\text{HMn}(\text{CO})_5$ where the product, $[(\text{CO})_5\text{Mn}]_2(\text{H})\text{Sn-Sn}(\text{H})[\text{Mn}(\text{CO})_5]_2$, contains an Sn-Sn as well as Sn-H bonds [148].

Rhenium hydrides have been used synthetically (eqns 7.78 and 7.79) [149, 150].

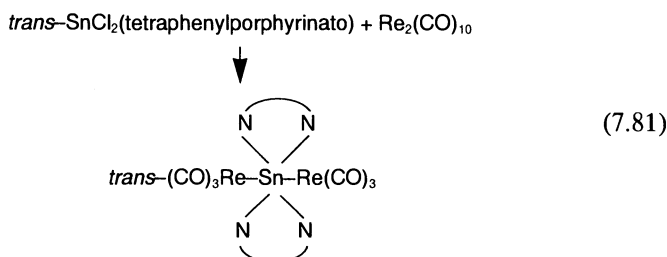
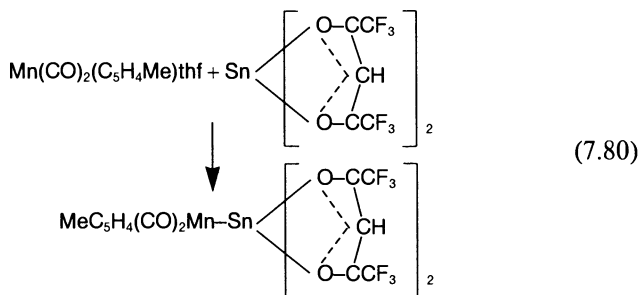


The anionic Mn hydride, $\text{K}[\text{MeC}_5\text{H}_4(\text{CO})_2\text{MnH}]$ reacts with Ph_2SnCl_2 giving

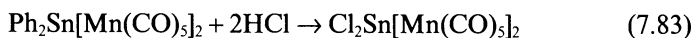
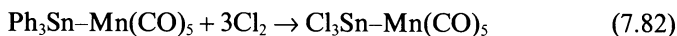
a bis-stannyl complex, $\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}(\text{SnPh}_2\text{Cl})_2$ and this type of reaction is markedly influenced by steric factors [151].

In these coloured Re complexes substitution of chlorine by methyl on tin lengthens the Re–Sn bond by 2 pm per methyl group; the two cyclopentadienyl rings are non-parallel [149].

A number of Mn(I)–Sn(II) complexes have been reported in which tin is bonded to a porphyrinato or β -diketonato ligand (eqns 7.80 and 7.81) [152, 153].



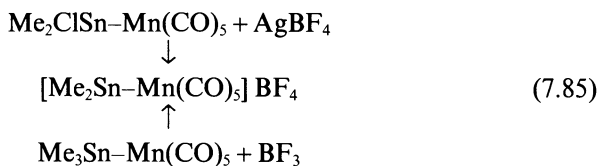
A striking feature of the chemistry of these complexes is their low chemical reactivity. Electrophiles commonly, though not invariably, cleave the Sn–C rather than the Sn–M bond, e.g. eqns 7.82–7.83 [154].



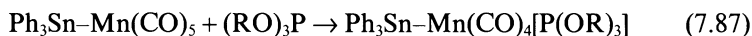
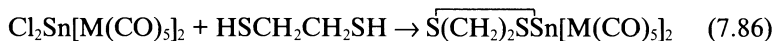
Redistribution of groups on tin occurs readily:



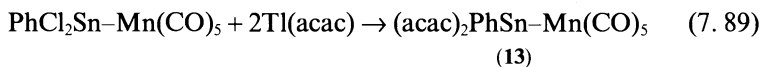
A further reflection of their low reactivity is the formation of cationic complexes (eqn 7.85) [155].



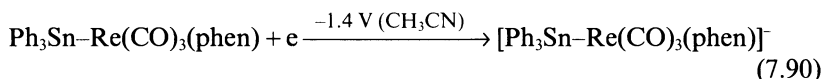
In compounds with tin-halide bonds the halide may be exchanged without Sn-M bond cleavage, and ligand substitution reactions at the transition metal occur readily, e.g. eqns 7.86–7.88 [133, 156, 157].



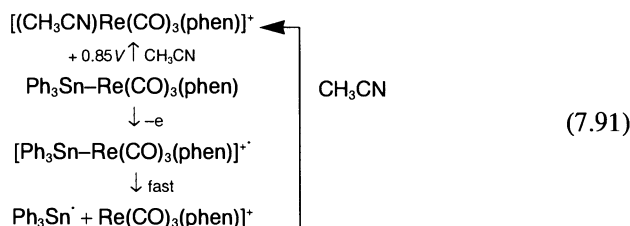
A number of ligand substitution reactions involving tertiary phosphines have been examined kinetically. The rate law is consistent with slow dissociation of CO followed by nucleophilic attack by the phosphine [158]. Most Sn(IV)-M complexes are four-coordinate about tin. However, in some acetonil-acetonates the tin is six-coordinate, and in (13) *cis*, *trans* and *fac* geometric isomers have been isolated [159].



In the acetolysis of $\text{Ph}_3\text{Sn-Mn}(\text{CO})_5$ and $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$, only Sn-Ph bonds are cleaved [160] and both SiHCl_3 and SnCl_4 react with $\text{Me}_3\text{Sn-Mn}(\text{CO})_5$ by chlorinative cleavage of one methyl group [161]. Similarly, reaction with Me_3SnCF_3 gives $\text{Me}_2(\text{CF}_3)\text{Sn-Mn}(\text{CO})_5$ [162]. $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ is reduced by LiAlH_4 to $\text{H}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ [163]. Many reactions of Sn-Mn and Sn-Re bonded complexes do result in Sn-M bond cleavage. Complexes of the type $\text{Ph}_3\text{Sn-Re}(\text{CO})_3(\text{phen})$ have a low-lying charge transfer excited state. The HOMO has sigma Sn-Re (or Sn-Mn) bonding character whilst the LUMO is mainly delocalized on the phenanthroline. Thus reduction is reversible since addition of an electron to the LUMO does not destabilize the Sn-Re bond:

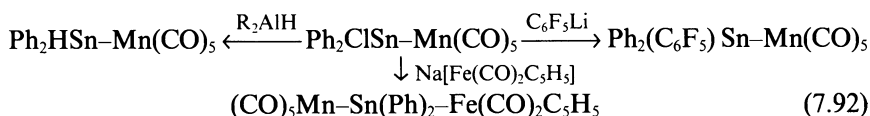


By contrast, oxidation is irreversible since it removes an electron from the HOMO [135]:

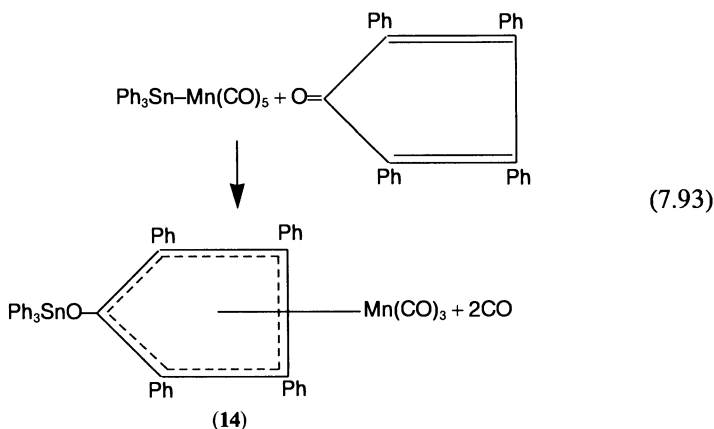


Electrochemical studies on compounds such as $(\text{CO})_5\text{Mn-SnPh}_3$ show that it undergoes a 2e oxidation with cleavage of the Mn-Sn bond. Reduction

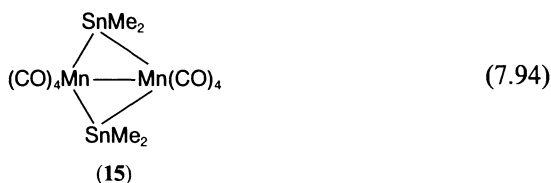
appears to be a net two-electron process yielding mainly $[\text{Mn}(\text{CO})_5]^-$ and $(\text{Ph}_3\text{Sn})^-$ [164]. The Sn–Mn bond in $\text{Me}_3\text{Sn–Mn}(\text{CO})_5$ is more readily cleaved than in the triphenyl analogue (due possibly to π -interaction of the phenyl groups strengthening the Sn–Mn bond) [155] and reagents which do so include RHgX , HgCl_2 , $\text{C}_2\text{H}_4\text{Br}_2$ [161], halogens, HX , ICl [155], Ph_2PCl and Ph_3PAuUCl [165]. Cleavage by bromine proceeds at a rate some 4000 times faster than for iodine. In other related reactions ICl forms a detectable charge transfer complex prior to bond cleavage. The rate of bond cleavage by iodine is mainly determined by the size of M (Mn , Re) and the effectiveness of shielding by other ligands [128, 129]. $\text{Ph}_2\text{ClSn–Mn}(\text{CO})_5$ reacts with various nucleophiles with retention of the Sn–Mn bond (eqn 7.92) [164].



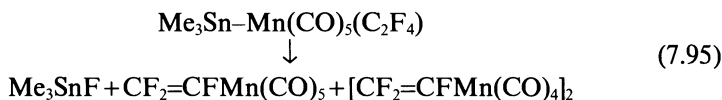
The reaction of $\text{Ph}_3\text{Sn–Mn}(\text{CO})_5$ with tetraphenylcyclopentadienone results in the formation of an Sn–O bond by transfer of Ph_3Sn from manganese to the ring with concomitant formation of the π -complex (14) (eqn 7.93) [166].



Reactions of these compounds with liquid sulphur dioxide show variations according to the groups bonded to tin. $\text{Ph}_3\text{Sn–M}(\text{CO})_5$ ($\text{M}=\text{Mn}$, Re) reacts by cleavage of Sn–C bonds giving a variety of structures in which SnOS(=O)Ph groups may be terminal or chelating. By contrast, the trimethyltin–manganese complex incorporates 1.5 mol of SO_2 whereas the rhenium analogue gives $(\text{CO})_5\text{Re–SnMe}_2[\text{OS(=O)Me}]$, the MeSO_2 ligand chelating the tin atom. With $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ 2 mol of SO_2 insert into Sn–C bonds and one Sn–Mn bond is cleaved [167]. Photolysis of $\text{Me}_2\text{ClSn–Mn}(\text{CO})_5$ gives the bridged dimer (15) as a sublimable solid [132, 168].



Difluorocarbene fails to insert into the Sn–Mn bond [162], but the reactions of perfluoroalkenes and alkynes are of some interest. UV irradiation facilitates the insertion of C_2F_4 into the Sn–Mn bond of $\text{Me}_3\text{Sn-Mn}(\text{CO})_5$ by what would seem to be a free radical mechanism, although the absence of products resulting from multiple insertions, i.e. $[\text{Me}_3\text{Sn}(\text{C}_2\text{F}_2)_n\text{Mn}(\text{CO})_5]$, is perhaps evidence against this. Other products can be accounted for by decomposition of the initially formed complex [157, 169] (eqn 7.95):



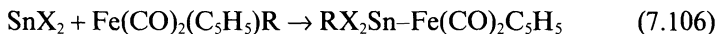
A similar reaction with $\text{ClFC}=\text{CF}_2$ gives evidence for non-selective insertion into the Sn–Mn bond (formation of Me_3SnCl and Me_3SnF). UV irradiation of $\text{Me}_3\text{Sn-Mn}(\text{CO})_5$ and $\text{CF}_3\text{CF}=\text{CF}_2$ (or $\text{CF}_2=\text{CFCF}=\text{CF}_2$) gives Me_3SnF together with *cis* and *trans* isomers of the alkene complex, $\text{CF}_3\text{CF}=\text{CFMn}(\text{CO})_5$ [or the *cis* isomer of $\text{CF}_3\text{CF}=\text{CFCF}=\text{CFMn}(\text{CO})_5$]. Perfluorocyclobutene reacts in a similar way [170]. The carbene complex *cis*- $\text{Ph}_3\text{Sn-Re}(\text{CO})_4[\text{C}(\text{OEt})\text{NR}_2]$ reacts with BI_3 by cleavage of Ph–Sn bonds, giving finally the $\text{I}_3\text{Sn-Re}$ complex [171].

7.8 Iron, ruthenium and osmium

Many papers have appeared in which these metals are bonded to tin and a large number of crystal structures have been reported. All of the metals bond to tin in either their 0 or +2 oxidation states with Lewis-base ligands completing the coordination at the transition metal. Tin may be in its +2 or +4 oxidation states with coordination numbers of two, four and less commonly five and six. In octahedral complexes like $(\text{Me}_3\text{Sn})_2\text{Os}(\text{CO})_4$, both *cis* and *trans* isomers have been isolated. Exchange of carbonyl groups between axial and equatorial positions is a non-dissociative process [172], and in favourable cases geometrical isomers can be identified from their IR spectra in the carbonyl region [173]. Preparative methods are similar for the three metals, and all of the methods employed have already been referred to in earlier parts of this chapter.

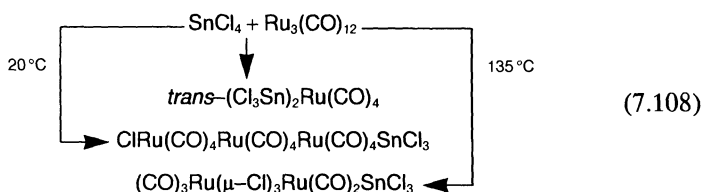
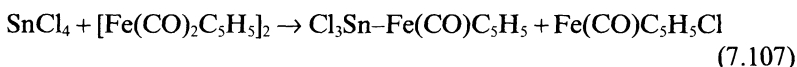
Syntheses often make use of anionic complexes of the transition metal as illustrated by the following examples [154, 174–176] (eqns 7.96–7.98).

Insertion of SnX_2 into Fe–C bonds (eqn 7.106) occurs readily via a radical chain process [187, 188].

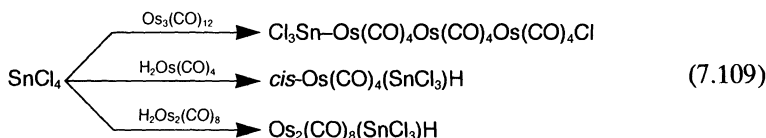


The complex $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$ reacts with AgBF_4 to form a crystalline borofluoride which, in the solid state, has one F of BF_4 close to tin: i.e. $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]_2\text{Sn}(\text{F})\text{BF}_3$ [189].

If $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ is dissolved in ethanol and CO passed into the solution followed by SnCl_2 , Ph_3P and acetone, the monomeric complex $\text{Cl}_3\text{Sn}-\text{RuCl}(\text{CO})(\text{Ph}_3\text{P})_2(\text{Me}_2\text{CO})$ is produced in which the phosphines are mutually *trans* and $[\text{SnCl}_3]$ is *trans* to Cl [190]. Insertion of SnCl_2 into the Ru–Cl bond of a stereoisomer of $\text{Ru}[\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2](\text{C}_5\text{H}_5)\text{Cl}$ occurs with retention of the geometry at the ruthenium atom. This means that SnCl_2 could attack at either chlorine or ruthenium, or both to give a three-centred transition state [191]. The complex $\text{RuCl}(\text{C}_6\text{H}_6)(\text{CH}_3)[\text{Ph}_2\text{PNHCH}(\text{CH}_3)\text{Ph}]$ is optically active, and reaction with SnCl_2 gives separable isomers in which the chirality at the ruthenium is different. The diastereoisomer, which is laevorotatory at 436 nm, has the R configuration, which is also the configuration of the chiral phosphine ligand [192]. The related cleavage of M–M bonds by SnX_4 (e.g. eqns 7.107 and 7.108) has also been used in synthesis [193], the products obtained often depending on the reaction conditions [194].



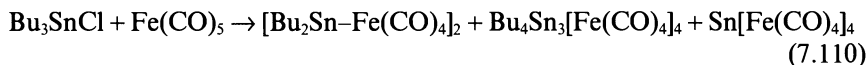
In $(\text{Me}_3\text{Sn})_2\text{Ru}_2(\text{CO})_8$, the Sn–Ru–Ru–Sn chain is almost linear [195]. Osmium carbonyls and carbonyl hydrides react with RSnX_3 or SnCl_4 forming Os–Sn bonds [196, 197] (eqn 7.109):



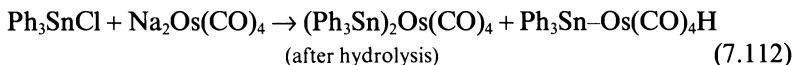
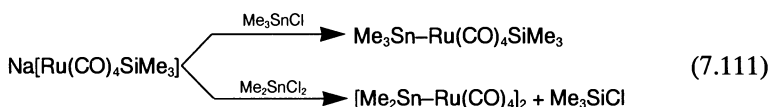
Sn–Ru(II) complexes are commonly five- or six-coordinate, depending on the nature of the other ligands present, e.g. $\text{R}_3\text{Sn}-\text{Ru}(\text{CO})_4\text{I}$ and $\text{R}_3\text{Sn}-\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}$.

Oxidative addition of SnCl_4 to $\text{Fe}(\text{CO})_4\text{PPh}_3$ gives $\text{Cl}_3\text{Sn}-\text{Fe}(\text{CO})_3(\text{PPh}_3)\text{Cl}$

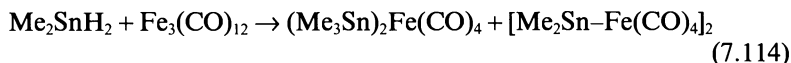
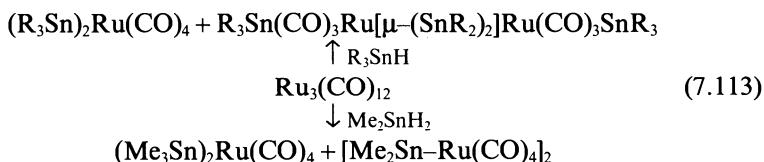
[198]. SnX_4 and $\text{Fe}(\text{CO})_5$ yield either $\text{Fe}(\text{CO})_4(\text{SnX}_3)\text{X}$ or *cis*- $\text{Fe}(\text{CO})_4(\text{SnX}_3)_2$, according to the experimental conditions; *trans*- $\text{Fe}(\text{CO})_4(\text{SnX}_3)_2$ isomerizes to the *cis* isomer in solution [199]. Oxidative addition products are formed in the reactions between organotin halides and neutral or anionic metal carbonyls and their derivatives [185] (eqn 7.110):



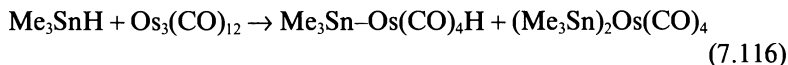
Similar reactions have been applied to the formation of ruthenium and osmium complexes [200, 201] (eqns 7.111 and 7.112).



Oxidative addition of organotin hydrides to the metal carbonyl (often with other ligands in place of some CO groups) occurs with displacement of CO and loss of hydrogen. With $\text{M}_3(\text{CO})_{12}$ more than one product may result by redistribution of the ligands about tin [200, 202, 203] (eqns 7.113–7.115).

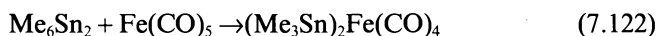
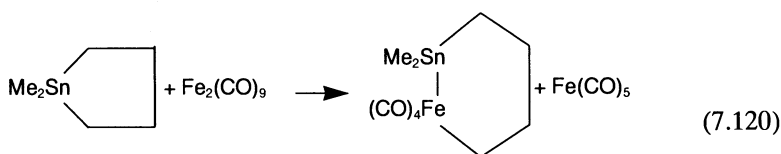
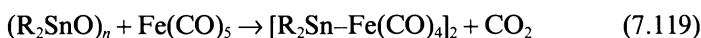
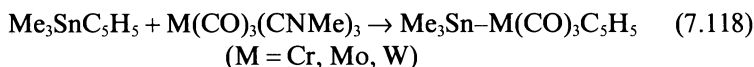
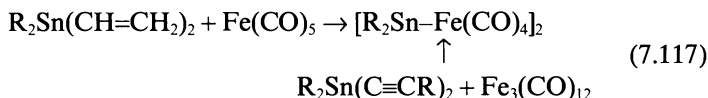


In the case of osmium, an Os–H bonded product can be isolated [197] (eqn 7.116):



The products of the reaction of Me_3SnH with $\text{Fe}(\text{CO})_5$ depend on the conditions employed: $(\text{Me}_3\text{Sn})_2\text{Fe}(\text{CO})_4$, $[\text{Me}_2\text{SnFe}(\text{CO})_4]_2$, $\text{Me}_4\text{Sn}_3[\text{Fe}(\text{CO})_4]_4$ and $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ have been isolated [204]. In its reaction with $\text{Os}_3(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)(\text{CO})_8\text{PMe}_2\text{Ph}$, Me_3SnH yields an HOs_3 product in which Me_3Sn is bonded to one external osmium atom of the Os_3 –sulphur cluster [205].

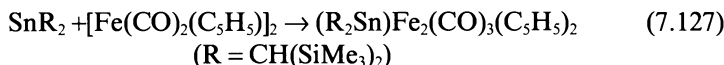
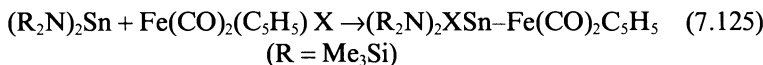
Oxidative addition of a wide range of R_4Sn , $R_2SnR'_2$, R_3SnR' and Sn_2R_6 compounds to transition metal complexes results in $Sn-M$ bond formation [206–211] (eqns 7.117–7.122):



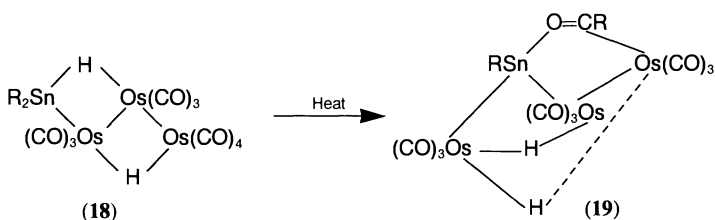
Tin-iron bonded compounds have been obtained from $Hg-Fe$ complexes by reaction with tin halides or by the action of $Hg-Sn$ compounds on iron complexes [118, 212] (eqns 7.123 and 7.124):



Stannylenes react in a variety of ways with complexes of these metals. Insertion into M -halide, $M-C$ and $M-M$ bonds can occur [48, 106] (eqns 7.125–7.127):

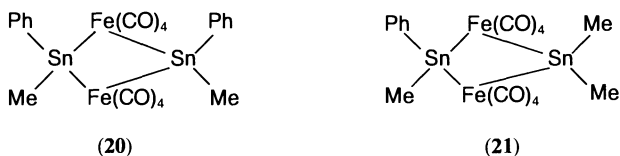


The reaction between R_2Sn [$R = (Me_3Si)_2CH$] and $Os_3H_2(CO)_{12}$ gives the complex $Os_3Sn(\mu-H)_2R_2(CO)_{10}$ (**18**) in which the Os_3Sn atoms form a closed plane with one hydrogen bridging an $Os-Sn$ bond and the other bridging an $Os-Os$ bond [213]. This complex transforms thermally into $RSnOs_3(\mu-H)_2(\mu-OCR)(CO)_9$ (**19**) via migration of a bulky R group from Sn to a carbonyl, giving the acyl complex [213]:



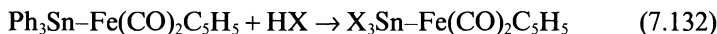
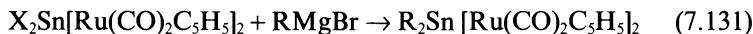
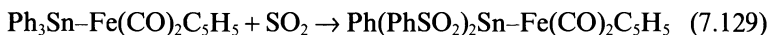
A further unusual structure is shown by $\text{Ph}_3\text{Sn}-\text{Fe}(\text{PEtPh}_2)_3\text{H}_3$: the three phosphines are mutually *cis* and the Ph_3Sn group caps the octahedral iron symmetrically about the three *cis*-Fe-H bonds [214]. Ru_3 clusters with just one *exo*- R_3Sn bond have also been isolated [215, 216].

The reaction between $(\text{C}_5\text{H}_5)_2\text{Sn}$ and $\text{Fe}_2(\text{CO})_9$ yields $[(\text{C}_5\text{H}_5)_2\text{Sn}-\text{Fe}(\text{CO})_4]_2$ in which the cyclopentadienyl rings are monohapto [217, 218]. The photochemically induced decomposition of $\text{PhMeSn}[\text{Fe}(\text{CO})_4]_2$ gives a mixture of two isomers, (20) and (21) which, from their NMR spectra, interconvert in solution by a combination of bridge deformation and iron-tin bond breaking [219].



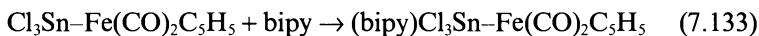
The ^{13}C NMR spectra of $(\text{Me}_3\text{Sn})_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) show that, for $\text{M} = \text{Fe}$ and Ru , they exist in solution as the *cis* isomers, whereas for $\text{M} = \text{Os}$ there is an appreciable amount of the *trans* isomer present. Isomerization is non-dissociative since $^{119}\text{Sn}-^{13}\text{C}$ CO coupling is retained [220]. In *cis*-(R_3Sn) $_2\text{Fe}(\text{CO})_4$ complexes, interchange of axial and equatorial CO groups occurs intramolecularly [221].

The low reactivity of these $\text{Sn}-\text{M}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) compounds is reflected in the large number of reactions in which the $\text{Sn}-\text{M}$ bond remains intact. Phosphines, R_3P [207, 222] and butadiene [223] will displace CO whilst other reagents attack $\text{R}-\text{Sn}$ or $\text{Sn}-\text{X}$ rather than $\text{Sn}-\text{M}$ bonds [122, 154, 183, 193, 224] (eqns 7.128–7.132).



However, Lewis bases cleave the $\text{Sn}-\text{Fe}$ bonds of dimeric structures [179]

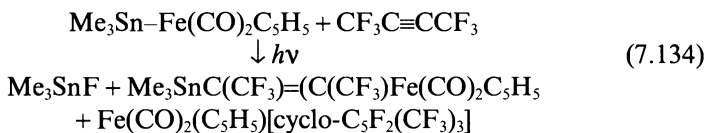
such as $(\text{CO})_4\text{Fe}[(\mu\text{-SnR}_2)]_2\text{Fe}(\text{CO})_4$, producing in solution monomeric $\text{R}_2\text{LSn-Fe}(\text{CO})_4$ reversibly [225]. In the osmium complex, $(\text{Bu}_2\text{PhSn})_2\text{Os}(\text{CO})_4$, only the Ph-Sn bonds are cleaved by HCl [226]. Reaction with chelating ligands such as 8-hydroxyquinoline and 2,2'-bipyridyl yields highly coloured complexes in which tin is six-coordinated [121], e.g. eqn 7.133.



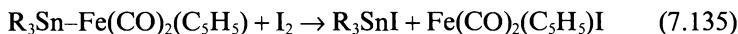
Tin(II) β -ketoenolates and $\text{Fe}_2(\text{CO})_9$ also give complexes which are six-coordinate about tin [227] whereas in (porphyrin) $\text{Sn-Fe}(\text{CO})_4$ the tin is five-coordinate [228].

In the reversible one-electron reduction of $\text{Ph}_3\text{M-Fe}(\text{CO})_2\text{C}_5\text{H}_5$ compounds ($\text{M}=\text{Si}, \text{Ge}, \text{Sn}$) the stability of the radical anion increases with the size of M [229]. Reduction of $(\text{R}_2\text{Sn})_2\text{Fe}_2(\text{CO})_8$ using NaH or Na/Hg in the presence of a Lewis base gives the stable dianion $[\text{R}_2\text{Sn-Fe}(\text{CO})_4]^{2-}$. This reduction can be considered as populating a non-bonding orbital on tin, with the possibility of some π -back-bonding to iron [230]. Electrochemical reduction of $\text{Cl}_3\text{Sn-Fe}(\text{CO})_2\text{C}_5\text{H}_5$ proceeds in two one-electron steps, only the first of which involves the X_3Sn groups, corresponding to the formation of X_3Sn^- and $[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]^-$ [231].

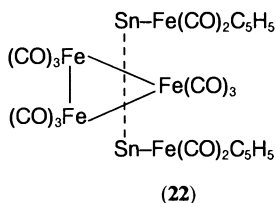
Reactions with fluoroalkenes and -alkynes are similar to those discussed under manganese, and usually result in cleavage of the Sn-M bond forming R_3SnF [170] (eqn 7.134).



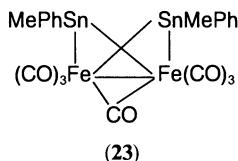
The iron-tin bond in $\text{R}_3\text{Sn-Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ complexes is cleaved by iodine (eqn 7.135) [129] whilst only one ruthenium-tin bond of $(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4$ is cleaved [232].



Photolysis of $\text{Me}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ results in loss of one CO , forming $\text{C}_5\text{H}_5(\text{CO})\text{Fe}[\mu\text{-(CO)-}\mu\text{-(Me}_2\text{Sn)}]\text{Fe}(\text{CO})\text{C}_5\text{H}_5$ [132]. The thermolysis of $[(\text{C}_5\text{H}_5)_2\text{Sn-Fe}(\text{CO})_4]_2$ results in transfer of cyclopentadienyl groups from tin to iron producing the metal cluster (22) [233].

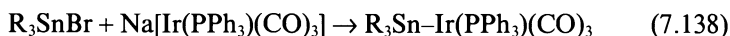
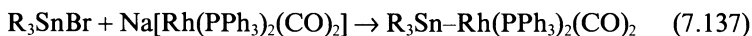


Photolysis of $[\text{PhMeSn-Fe(CO)}_4]_2$ gives $(\text{PhMeSn})_2\text{Fe}_2(\text{CO})_7$ (**23**); NMR evidence is consistent with three isomeric forms of this compound resulting from the relative positions of the methyl and phenyl groups [234].



7.9 Cobalt, rhodium and iridium

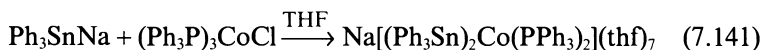
All three transition metals form complexes with tin. For cobalt, the metal is mostly in its +1 oxidation state, whereas for rhodium both the +1 and +3 states form Sn-bonded complexes, and with iridium there is in addition a Sn-Ir(V) complex. Coordination numbers of four, five and six are found for the transition metals. Tin in these complexes may be in its +2 or +4 oxidation states with coordination numbers of three or four, or six in the case of chelate complexes. The tendency of these metals to form cluster compounds makes an interesting structural chemistry, though relatively few reactions have been studied beyond ligand exchange and electrophilic substitution at either metal. The question of $d\pi-d\pi$ bonding between tin and cobalt has been considered in relation to data from various physicochemical methods. The tentative conclusion, not surprisingly, is that the π -interaction is non-zero, and that R_3Sn is a stronger σ -donor than Cl_3Sn [235]. Reactions of complex anions of the transition metal form the basis of many syntheses, e.g. eqns 7.136–7.139 [236–238]



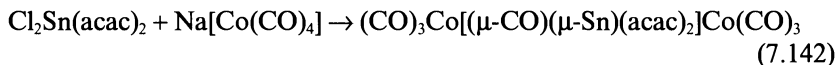
Although complexes with PF_3 ligands are poor nucleophiles, Sn-M (M = Rh, Ir) bonded complexes have been isolated (eqn 7.140); the corresponding reactions with silicon or germanium are unproductive [239].



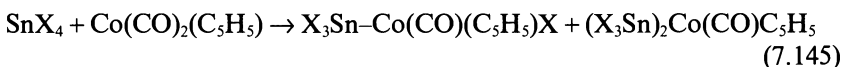
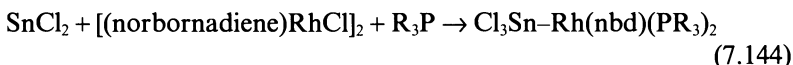
Nucleophilic substitution reactions on the transition metal halides have been used to form Sn-M bonds [240].



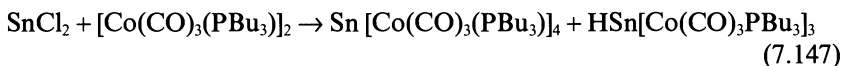
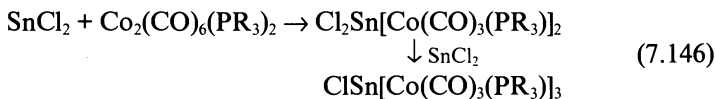
With chelating ligands on tin, six-coordinate Sn(IV) complexes result [241]:



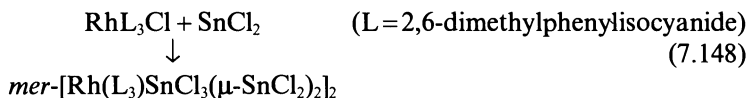
Reactions of SnX_2 and SnX_4 compounds with carbonyl, substituted carbonyl, or alkene derivatives of these metals result in Sn-M bond formation [242–244] (eqns 7.143–7.145).



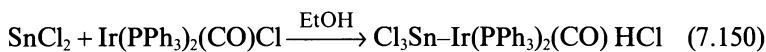
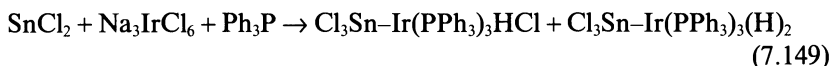
The reaction of SnCl_2 with Co-Co complexes occurs in two stages [245] and reactions of this type can result in unexpected products [246] (eqns 7.146 and 7.147).



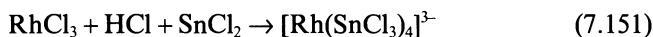
As with cobalt, synthetic reactions using SnCl_2 and rhodium complexes often result in products in which (depending on the nature of other ligands present) SnCl_2 or even SnCl bridge two transition metals [247] e.g. eqn 7.148, where the product consists of two edge-sharing octahedrally coordinated Rh atoms linked by two bridging SnCl_2 groups.



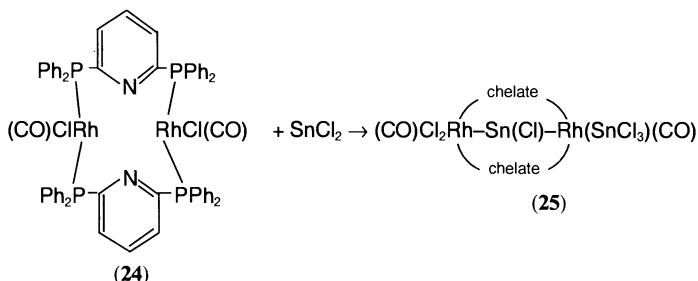
SnCl_2 and Ir(III) complexes form a range of $\text{Cl}_3\text{Sn-Ir(III)}$ hydride products, the hydrogen coming from the solvent [EtOH or $\text{MeO}(\text{CH}_2)_2\text{OH}$] [248] (eqns 7.149 and 7.150):



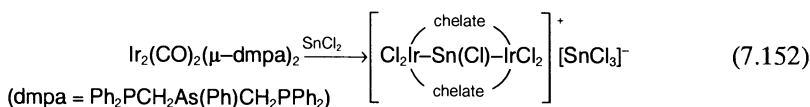
In its +3 oxidation state, rhodium is reduced to rhodium(I) by SnCl_2 in acid solution to give coloured anionic complexes [249, 250] (eqn 7.151).



The Rh(I) complex (**24**) undergoes a very unusual reaction with SnCl_2 giving a product (**25**) in which one Rh has been oxidized to Rh(III) and SnCl bridges both Rh atoms [251].

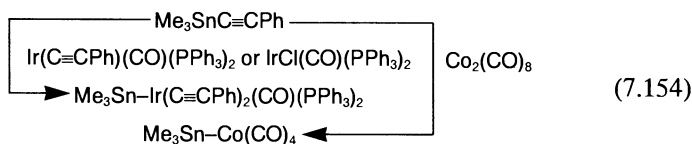
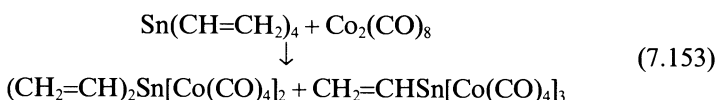


The somewhat similar Ir reaction (7.152) yields a product with Sn(Cl) bridging two Ir atoms [252].

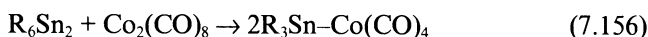
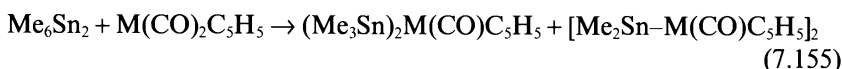


SnCl_4 reacts with $\text{Co}(\text{PMe}_3)_2\text{C}_5\text{H}_5$ to form a 1:1 adduct at -70°C which, with excess SnCl_4 , is converted into $[\text{Cl}_3\text{Sn}-\text{Co}(\text{PMe}_3)_2\text{C}_5\text{H}_5]^+[\text{SnCl}_5]^-$ [253]. Reaction of Me_2SnCl_2 or MeSnCl_3 with $\text{Co}_2(\text{CO})_8$ gives the mixed tetrahedral metal clusters $\text{MeSnCo}_3(\text{CO})_9$ [254] and $\text{MeSn}[\text{Co}(\text{CO})_4]_3$ [255].

Cleavage of tin-carbon bonds gives Sn-M complexes as in the following examples [255, 256] (eqns 7.153 and 7.154):



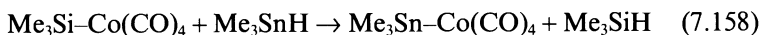
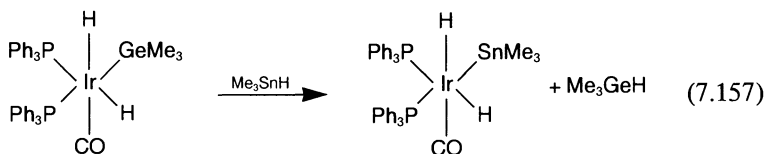
Likewise di-tin compounds oxidatively add to M(0) and M(I) complexes [257] (eqns 7.155 and 7.156):



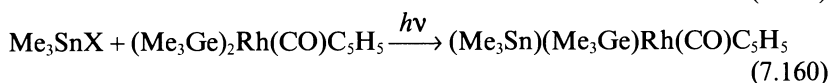
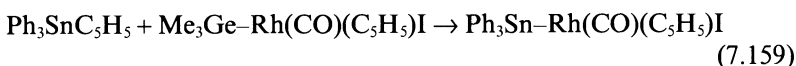
Reaction between Me_3SnH and $\text{Co}_2(\text{CO})_8$ gives [258] hydrogen and $\text{Me}_3\text{Sn}-\text{Co}(\text{CO})_4$.

The reactivity of Sn-H compounds towards iridium(I) is markedly dependent on the groups bonded to both tin and iridium. Thus the oxidative addition of trimethyltin hydride to *trans*-Ir(PPh₃)₂(CO)Cl gives an Ir(III) product as a colourless crystalline solid whose ¹H NMR spectrum suggests the presence of isomeric forms of Me₃Sn-Ir(PPh₃)₂(CO)(Cl)H and Me₃Sn-Ir(PPh₃)₂(H)₂(CO) in solution. Bu₃SnH also undergoes a complex reaction with the same iridium complex. The tetrakis complex Sn{Co(CO)₃PR₃}₄ is formed as a red powder by electroreduction of Co₂(CO)₆(PR₃)₂/Bu₄NPF₆ using a tin anode; compounds of this type have catalytic properties in relation to alkene hydroformylation [259].

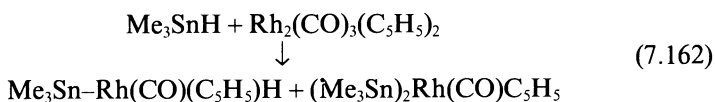
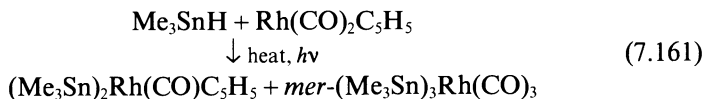
Trimethyltin complexes of cobalt(I) and iridium(III) are readily obtained by exchange reactions [260] (eqns 7.157 and 7.158).



Other types of exchange reactions may be used to form tin-rhodium bonds [261]:



Oxidative addition of R₃SnH to *trans*-IrCl(CO)(PPh₃)₂ gives the Ir(III) complex R₃Sn-Ir(PPh₃)₂(CO)HCl [262]. The related reactions with Rh(I) are rapid and exothermic. Use of Me₃SnH only affords decomposition products, but Bu₃SnH and Rh(PPh₃)₃Cl give the five-coordinated complex, Bu₃Sn-Rh(PPh₃)₂HCl [263]. With other rhodium(I) complexes, reactions of Me₃SnH (eqns 7.161, 7.162) can be more satisfactorily controlled [261].



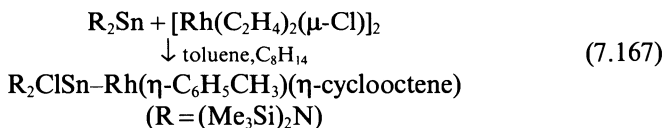
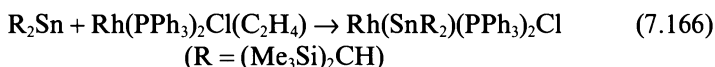
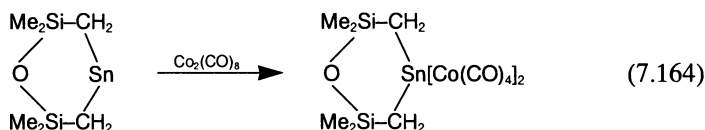
Few reactions of organotin dihydrides have been examined. The reaction of Me₂SnH₂ with Co₂(CO)₈ gives the bridged product

$(\text{CO})_3\text{Co}[(\mu\text{-SnMe}_2)_2]\text{Co}(\text{CO})_3$ as a bright yellow solid (eqn 7.163). In this complex, rapid exchange of axial and equatorial CO groups occurs even at low temperature, and exchange of methyl group positions takes place in a concerted fashion [264].

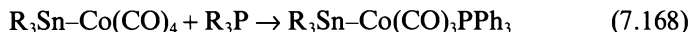


Intramolecular exchange of axial and equatorial CO groups also occurs readily in five-coordinated complexes, $\text{R}_3\text{SnCo}(\text{CO})_4$. In general, the barrier to exchange seems to correlate with the size of the R groups [265]. The oxidative addition of Ph_3SnH to $\text{Ir}(\text{PPh}_3)_3(\text{CO})\text{H}$ proceeds by dissociation of phosphine and *cis* addition of Sn–H giving $\text{Ph}_3\text{Sn-Ir}(\text{PPh}_3)_2(\text{CO})(\text{H})_2$ [266].

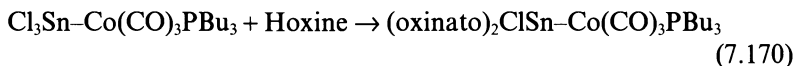
Stannylenes, R_2Sn , have been used in forming Sn–Co bonds. In the majority of cases they behave as Lewis bases, although products of oxidative addition are formed in some reactions [106, 124, 267, 268] (eqns 7.164–7.167):



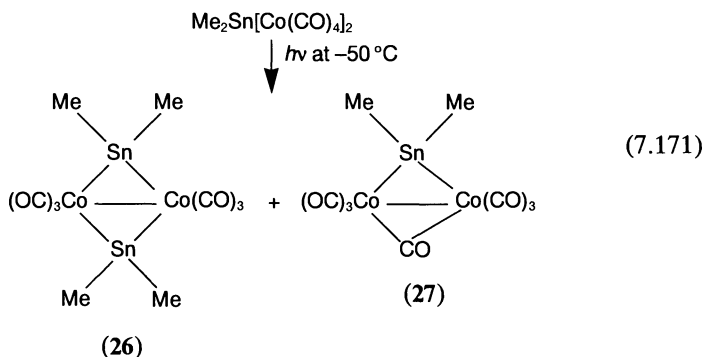
Ligand exchange and alkylation reactions can be carried out without cleaving the Sn–M bond [269, 270]:



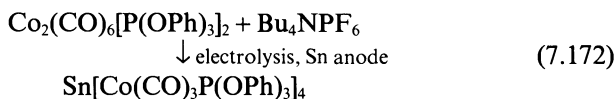
A number of the 16-electron Sn–M complexes will reversibly add a Lewis base, e.g. $\text{Ph}_3\text{Sn-Co}(\text{PMe}_3)_3$ adds 1 mole of Me_3P [271]. In $\text{Me}_3\text{SnCo}(\text{CO})_3\text{L}$ ($\text{L} = \text{Ph}_3\text{P}$, Ph_3As) the Co has a trigonal bipyramidal geometry with axial Me_3Sn and L ligands [272]. $\text{X}_3\text{Sn-Co}$ complexes react with chelating ligands such as 8-hydroxyquinoline to give six-coordination at tin [121] (eqn 7.170):



Photolysis of the stannylene complex, $\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, results in the formation of (26) and (27) [132] (eqn 7.171):



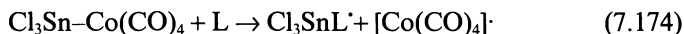
Electrolytic synthetic methods have been successfully applied in several cases [273] (eqn 7.172).



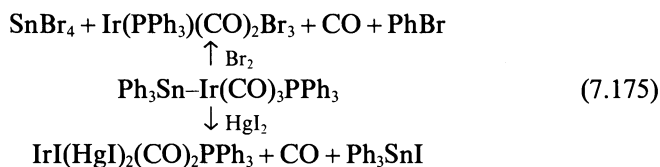
The tin-cobalt bond in $\text{Me}_3\text{Sn}-\text{Co}(\text{CO})_4$ is cleaved by halogens, Me_2AsCl , Ph_2PCl and Ph_3AuCl . In all cases Me_3SnX and a $\text{Co}(\text{I})$ complex are formed. In complexes with more than one bond between tin and M the reaction with iodine can be controlled, cleaving only one $\text{Sn}-\text{M}$ bond as in eqn 7.173 [235, 236].



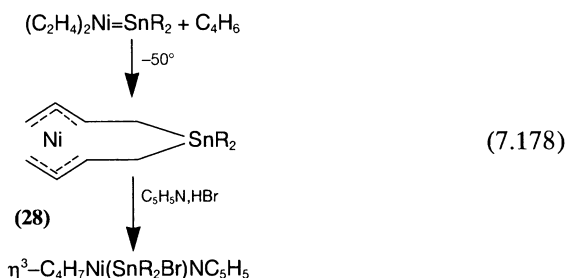
Fluoroalkenes insert into the $\text{Sn}-\text{Co}$ bond [274] and the $\text{Sn}-\text{Co}$ bond in $[\text{R}_3\text{Sn}-\text{Co}(\text{PMe}_3)_2\text{C}_5\text{H}_5]\text{Cl}$ is cleaved by HgCl_2 to give Me_3SnCl [253]. The reaction of $\text{Cl}_3\text{Sn}-\text{Co}(\text{CO})_4$ with tertiary phosphines and arsines (L) results in tin-cobalt bond cleavage and formation of an ionic complex $[\text{Co}(\text{CO})_3\text{L}_2][\text{SnCl}_3]$, with good evidence that these reactions proceed by a radical chain mechanism, since they are sensitive to oxygen and radical scavengers. The kinetics have been interpreted, in terms of a series of 14 reactions of which the first is shown in eqn 7.174 [275].



The tin-iridium bond in iridium(I) complexes is cleaved by electrophiles [237] (eqn 7.175):

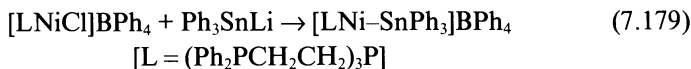


An interesting compound is the 16-electron Ni(0) complex $(C_2H_4)_2Ni=SnR_2$ [$R=(Me_3Si)_2CH$]; it undergoes some alkene substitution reactions without affecting the Sn–Ni bond (e.g. with 1,6-heptadiene), but with butadiene, oxidation of both Sn and Ni occurs forming **(28)**. Reaction of **(28)** with pyridine/HBr results in the reformation of a Ni–Sn(IV) bond with loss of C_4H_8 [281] (eqn 7.178).



$\text{R}_3\text{Sn-Ni}(\text{CO})\text{C}_5\text{H}_5$ and related compounds have been obtained from R_3SnCl and $\text{NaNi}(\text{CO})\text{L}$ where $\text{L} = \text{C}_5\text{H}_5$ or C_5Me_5 [282, 283].

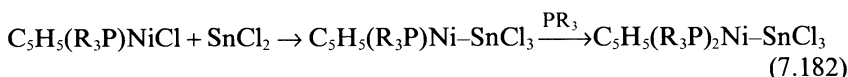
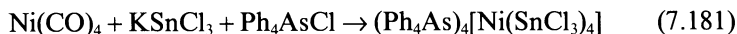
Five-coordinated trigonal bipyramidal nickel(II) cations of the type $[\text{LNi-SnPh}_3]^+$ have been formed by similar nucleophilic substitution reactions (eqn 7.179).



Cationic complexes of these types are diamagnetic and fairly air-stable [284]. A further synthetic method for nickel(II) complexes which is of wide applicability involves the cleavage of Sn-Sn bonds [116] (eqn 7.180):

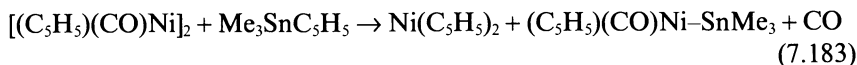


Both nickel(0) and nickel(II) complexes have been isolated containing Ni-SnCl₃ and Ni-SnCl₂-Ni groups (eqns 7.181 and 7.182).

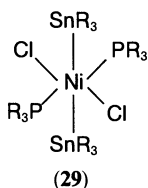


Ni(II)-Sn complexes are coloured (brown, gold or green) and mostly decompose between 100 and 150 °C in the absence of air [7].

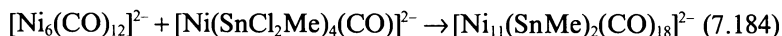
The Ni(0)-SnCl₃ complex is oxidized by air both in the solid state and in solution, and there is evidence for reversible dissociation in solution into SnCl₂ and the complex anion $[\text{NiCl}_4]^{4-}$. The high reactivity of the Sn-cyclopentadienyl bond may be used to form Ni-Sn complexes [285] (eqn 7.183).



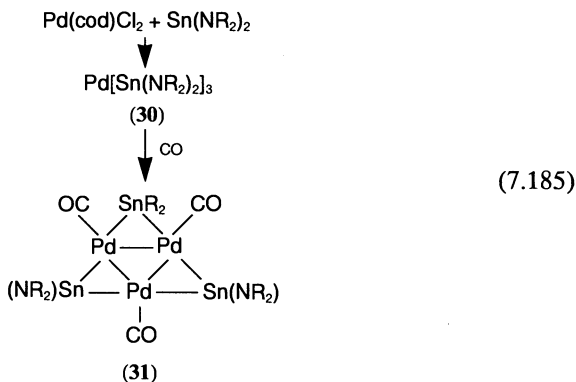
Reaction between $\text{Ni}(\text{Ph}_3\text{P})_3$ and Me_3SnCl or Ph_3SnCl in toluene leads to the isolation of low-spin Ni(IV) complexes which are colourless, stable in air and inert towards substitution by $(\text{Ph}_2\text{PCH}_2)_2$, and probably have the configuration (29) [286].



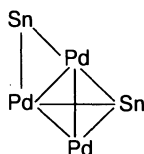
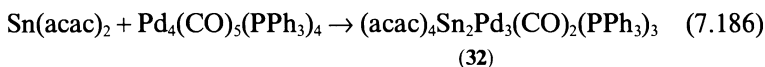
Icosahedral nickel clusters, $1,12\text{-Sn}_2\text{Ni}_{10}$, with an additional nickel atom at the centre of the icosahedron, are among the most remarkable complexes in this area of chemistry [287] (eqn 7.184).



Both organotin-Pd and $\text{X}_3\text{Sn-Pd}$ have been described with palladium in its zero, +1 and +2 states and tin in its +2 and +4 oxidation states. The palladium(II) complex $\text{Pd}(\text{cod})\text{Cl}_2$ (cod = cycloocta-1,5-diene) reacts with the stannylene $\text{Sn}(\text{NR}_2)_2$ ($\text{R} = \text{Me}_3\text{Si}$) to give, surprisingly, the Pd(0) complex (30), probably via $\text{Pd}[(\text{cod})\{\text{Sn}(\text{NR}_2)_2\text{Cl}\}_2]$ which undergoes reductive elimination in the presence of excess $\text{Sn}(\text{NR}_2)_2$ [288]. The platinum analogue reacts similarly. In (30) palladium, tin and nitrogen all have trigonal planar coordination. Both the Pd and Pt complexes are extremely air-sensitive. On reaction with CO, (30) forms the cluster (31), in which the stannylene $\text{Sn}(\text{NR}_2)_2$ functions as a bridging group between adjacent Pd atoms (eqn 7.185).

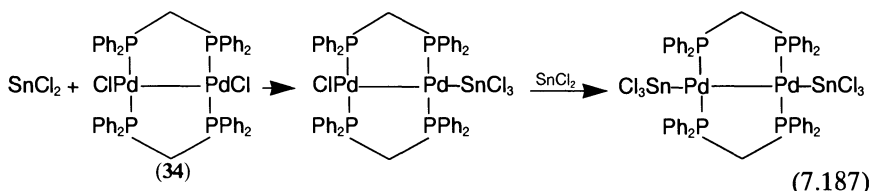


This cluster undergoes a reversible single electron reduction in THF, and at more negative potentials two further reductions. The radical anion initially generated decomposes in THF at -40°C to yield a paramagnetic product that contains two equivalent tin nuclei [289]. $(\eta^3\text{-C}_3\text{H}_5)\text{ClPd}(\text{SnR}_2)_2$, a dark yellow solid decomposing at 80°C , is formed from $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ and $\text{Sn}(\text{NR}_2)_2$ ($\text{R} = \text{Me}_3\text{Si}$) [48]. In general, palladium clusters react with Sn(II) compounds to form new metal clusters, sometimes with displacement of palladium as well as neutral ligands, for example (eqn 7.186):

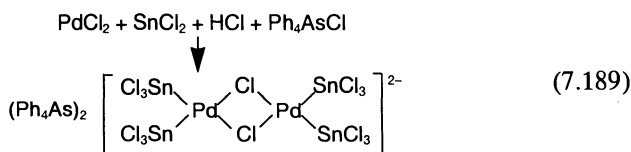
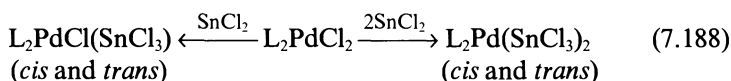


(33)

In (32), the $[\text{Pd}_3\text{Sn}_2]$ core has a propeller-shaped framework (33) [290]. SnCl_2 will insert into one or both of the $\text{Pd}-\text{Cl}$ bonds in the complex (34) [291] (eqn 7.187).



Palladium(II)-Sn complexes have been obtained by insertion of SnCl_2 into $\text{Pd}-\text{Cl}$ bonds yielding both neutral and anionic complexes ($\text{L}=\text{Ph}_3\text{P}$, etc.) [7, 292–294] (eqns 7.188–7.190).



However, an excess of SnCl_2 reacts with $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ in benzene or THF to give ultimately the decomposition products Pd, SnCl_4 and allyl [295].

The $\text{Pd}-\text{Sn}$ bonds in compounds of these types are cleaved by iodine, and in solution, phosphine- and arsine- $\text{Pd}-\text{SnCl}_3$ complexes undergo rapid phosphine or arsine exchange at room temperature, in contrast to the analogous Pt complexes [292]. In $\eta^3\text{-C}_3\text{H}_5(\text{Ph}_3\text{P})\text{Pd}-\text{SnCl}_3$, the $\text{Pd}-\text{Cl}$ distance of 256 pm is about 10 pm less than the sum of the covalent radii [7].

Platinum-tin chemistry has been extensively explored and has produced extremely novel structures. Complexes have been studied with platinum in zero, +2 and +4 and tin in its +2 and +4 oxidation states. Neutral, anionic and cationic complexes have been identified, often in the form of metal cluster compounds. $\text{Pt}(0)-\text{Sn}$ complexes are four-coordinated (tetrahedral) about

platinum; those of Pt(II) are four-(planar) or five-(trigonal bipyramidal) coordinated, whilst Pt(IV)–Sn complexes are octahedrally coordinated about platinum.

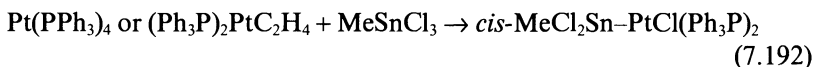
Cationic Pt(II)–SnCl₃ complexes were first prepared in 1835, although it was years before they were recognized as such. The original paper (On some combinations of protochloride of platina with protochloride of tin) describes how ‘these bodies unite in two different proportions; that containing least tin is of an olive brown colour, crystalline and very deliquescent, decomposed by water . . . The second which contains most tin is of an intensely red colour, soluble in water giving a splendid red solution . . . The colour of the solution was found by Professor Kane, on examination by a prism, to be an absolutely homogeneous red’ [296]. The formation of a red complex in this way is the basis of a standard qualitative test for platinum in aqueous solution [297].

Examples of Pt(0)–Sn compounds include the trigonal complex Pt[Sn{N(SiMe₃)₂}]₃, which is isomorphous with the corresponding palladium complex already described [298, 299]. It is formed from Pt(cod)₂ and the stannylene in toluene. An orange Sn(II)–Pt(0) complex [(acac)₂Sn]₂Pt(PPh₃)₂ with tetrahedral geometry about platinum is formed from Pt(PPh₃)₂ and Sn(acac)₂. With excess acetylacetone a more complex metal cluster results [300]. In the reaction of SnR₂ [R = (Me₃Si)₂CH] with PtCl₂(PEt₃)₂, or (better) [PtCl₂(PEt₃)]₂, one SnR₂ coordinates as a Lewis base whilst the other inserts into a Pt–Cl bond giving (R₂Sn)(R₂ClSn)Pt(PEt₃)Cl [106]. By contrast, (R₂N)₂Sn and (cod)PtCl₂ give the Sn(IV) complex, (cod)Pt[SnCl(NR₂)₂]₂ [48, 106, 288, 298].

The oxidative addition of R₃SnX and R₂SnX₂ to Pt(0) was originally thought to involve the formation of a Pt–X bond, but in most cases this is not so. R₃SnCl reacts with (Ph₃P)₂Pt(C₂H₄) by displacement of ethene and insertion of platinum into an Sn–C bond [301] (eqn 7.191).

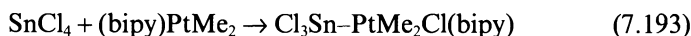


Ph₂SnCl₂ reacts in the same way, but Me₂SnCl₂, PhSnCl₃, MeSnCl₃ and SnCl₄ react by insertion of platinum into an Sn–Cl bond [302] (eqn 7.192).



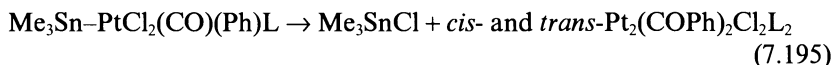
In other cases three-coordinate Pt(0) complexes yield a five-coordinated Pt(II) product without ethene elimination [303].

Oxidative addition of SnCl₄ or MeSnCl₃ to chelated Pt(II) yields six-coordinated Pt(IV) complexes [304] (eqns 7.193 and 7.194).

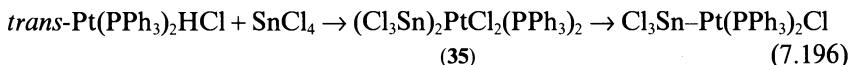


The reaction of *cis*-Pt(CO)LCl₂ (L = R₃P) with Me₃SnPh probably proceeds through an oxidative addition stage which is followed by phenyl

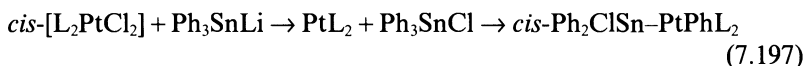
migration and elimination of Me_3SnCl yielding a Cl-bridged complex [305] (eqn 7.195).



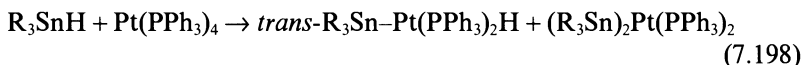
In reactions of platinum hydridohalides with SnCl_4 , hydrogen chloride is eliminated and the initially formed Pt(IV) complexes e.g. (35) readily undergo reductive elimination [306] (eqn 7.196).



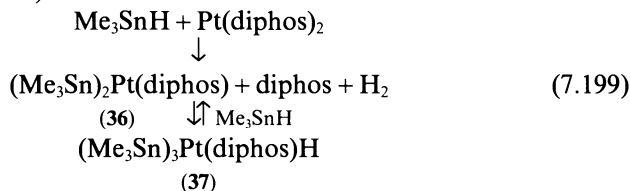
Many reactions originally thought to be simple are proved far more complex when examined by ^{31}P NMR. For example, the reaction of $\text{Me}_3\text{SnNMe}_2$ with PtL_2HCl gives at least three products rather than just that expected from the elimination of Me_2NH . Loss of HCl generates PtL_2 which then adds Me_3SnCl to give $\text{Me}_2\text{ClSn-PtMeL}_2$. Even nucleophilic substitution reactions are often complex for similar reasons [301, 305] (eqn 7.197).



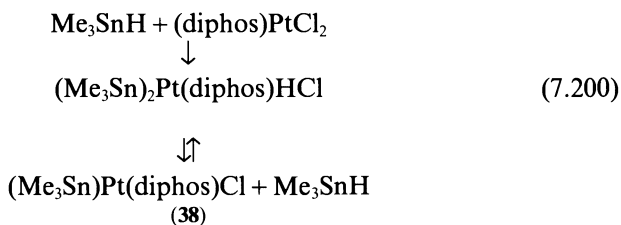
The report that $\text{Ph}_3\text{Sn-Pt}(\text{PPh}_3)_2\text{Cl}$ decomposes in hot acetone to $\text{Pt}(\text{PPh}_3)_2\text{PhCl}$ [306] is incorrect, and can also be ascribed to these effects [301]. Oxidative addition of organotin hydrides occurs readily both to Pt(0) and to Pt(II) complexes [307, 308] (eqn 7.198)



The related reaction with $\text{Pt}(\text{diphos})_2$ [diphos = $(\text{Ph}_2\text{PCH}_2)_2$] proceeds first to the Pt(II) complex (36) and in the presence of excess hydride to the Pt(IV) complex (37) (eqn 7.199).

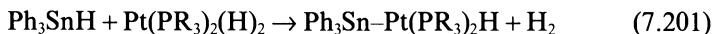


Similarly, platinum(II) complexes and Me_3SnH yield the Pt(IV) product which dissociates reversibly in solution to (38) (eqn 7.200)

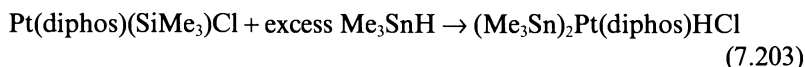
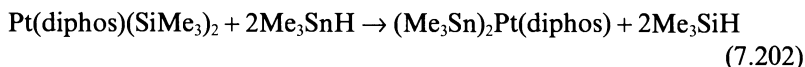


The stereochemistry of these Pt(IV) complexes with unidentate phosphine ligands is readily determined from their ^1H and ^{31}P NMR spectra [301, 302]. The reaction between R_3SnH and the carbonato complex $\text{Pt}(\text{PMe}_3)_2(\text{CO}_3)$ gives $(\text{R}_3\text{Sn})_2\text{Pt}(\text{PMe}_3)_2(\text{H})_2$ with a *cis*-[H–Pt–H] and *trans*-[P–Pt–P] configuration. In benzene this complex loses H_2 reversibly giving *trans*- $(\text{R}_3\text{Sn})_2\text{Pt}(\text{PMe}_3)_2$ [309].

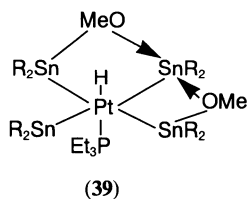
The extent and rate of these addition reactions can be controlled using bulky phosphines such as tricyclohexylphosphine. If a very bulky phosphine is used, no reaction occurs. In the case of a Pt-dihydride complex, hydrogen is eliminated [310] (eqn 7.201).



Platinum–tin bonds are formed by the exchange reactions of Pt–Si or Pt–Ge bonded complexes with Me_3SnH . These are equilibrium reactions where the Pt–Sn product is strongly favoured [311] (eqns 7.202 and 7.203).

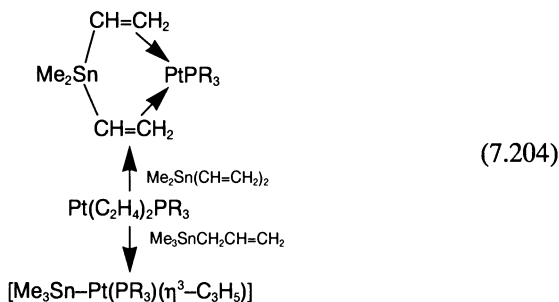


Most unexpectedly, the Sn–Pt(IV) complex (39) is formed in the reaction of (carbonato)Pt(SET₂)(PR₃) with (*p*-tolyl)₃SnH in methanol.



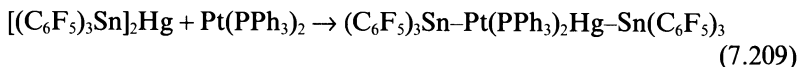
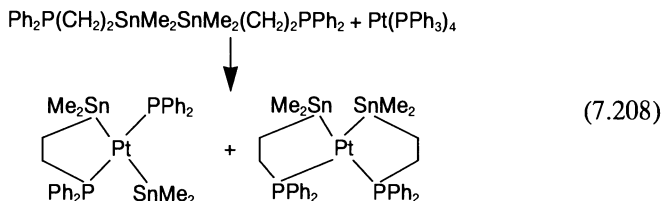
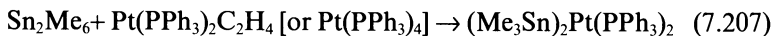
This highly unusual structure involves three Sn(IV) ligands (R_3Sn and two R_2SnOMe) and one stannylene (R_2Sn) in which the tin is five-coordinate due to coordination of lone-pair electrons from the two methoxy groups [312].

The reaction of tin–carbon bonds with Pt(0) complexes can take various forms [256, 301, 313] (eqns 7.204–7.206).



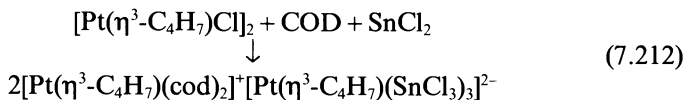
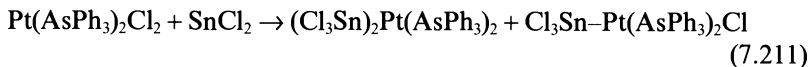
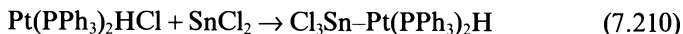


Ditin and mercury-tin compounds will also add to Pt(0) [308, 314, 315] (eqns 7.207–7.209).



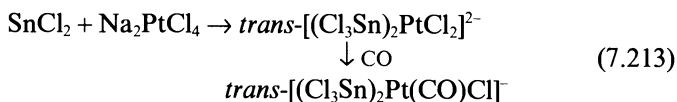
The 'mixed' compound $\text{R}_3\text{SnHgGeR}_3$ reacts in the same way, selectively forming an Sn-Pt bond.

Insertion of SnCl_2 into Pt-Cl bonds has already been referred to. The chemistry of this reaction has been extensively studied because some of the products act as catalysts for the homogeneous hydrogenation and isomerization of alkenes. Neutral and anionic complexes with one to three SnCl_3 groups may be produced [306, 316, 317] (eqns 7.210–7.212).



When these reactions are carried out in acid solution, anionic complexes are formed [318].

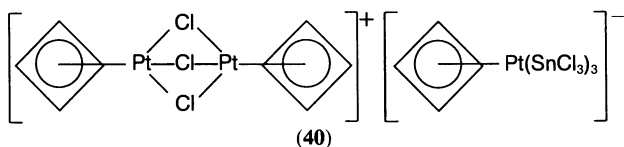
Five-coordinate cationic complexes such as $[\text{L}_4\text{PtSnCl}_3][\text{BPh}_4]$ are also known [292]. Similar anionic complexes are formed from SnCl_2 and PtCl_2 or Na_2PtCl_4 [319, 320] (eqn 7.213).



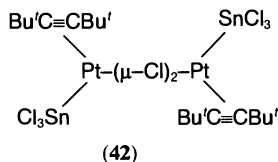
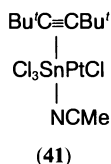
If a platinum(IV) compound is used in this type of reaction, reduction to platinum(II) occurs. Many of these anions are five-coordinate and, if combined with large cations, may be obtained as crystals. Examples are

$[(\text{Cl}_3\text{Sn})_5\text{Pt}]^{3-}(\text{PMePh}_3)_3$ and $[(\text{Cl}_3\text{Sn})_4\text{PtH}]^{3-}(\text{NMe}_4)_3$ [249]. The reaction between K_2PtCl_4 , Me_4NCl and SnCl_2 in acetone gives a cluster compound with the probable structure $(\text{Me}_4\text{N})_4[(\text{Cl}_3\text{Sn})_6\text{Pt}_3(\mu^3\text{-SnCl})_2]$, i.e. with the two $[\text{SnCl}]$ groups lying above and below a triangle of platinum atoms [289]. Similar anionic clusters are formed from SnCl_2 and PtCl_2 [319, 320] and the reaction of SnCl_2 with $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ gives the remarkable anion $[\text{Pt}_8(\text{SnCl}_2)_4(\text{CO})_{10}]^{2-}$ [321].

Ethyne and other alkynes react with $\text{Pt}(\text{MeCN})_2\text{Cl}_2$ in the presence of SnCl_2 , forming (40) in which ethyne, dimerized to cyclobutadiene, remains coordinated to platinum:



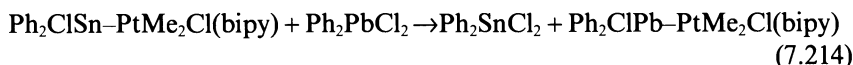
Heating this ionic complex with HCl /acetone results in loss of all the tin from the anion as SnCl_2 . With sterically hindered alkynes, dimerization does not occur and the reaction stops at the stage of mono- and dimeric products (41) and (42) [322]. Hexafluorobutyne inserts into the Pt-Sn bond of $[\text{Et}_3\text{PPt}(\text{SnCl}_3)(\mu\text{-Cl})_2]$ forming $[\text{Cl}_3\text{Sn}(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{Pt}(\text{PET}_3)(\mu\text{-Cl})_2]$ [323].



$(\text{cod})_3\text{Pt}_3(\text{SnCl}_3)_2$ has a trigonal bipyramidal structure with axial SnCl_3 groups, each equatorial platinum atom being chelated to a diene [320].

Many electrophilic reagents e.g. $\text{PhC}\equiv\text{CH}$, $\text{CH}_3\text{CO}_2\text{H}$, HCl , $\text{HOCH}_2\text{CH}_2\text{SH}$, SnCl_4 , I_2 , CH_3I , CCl_4 and HgCl_2 cleave one or both of the tin-platinum bonds in the complex $(\text{Me}_3\text{Sn})_2\text{Pt}(\text{CH}_2\text{PPh}_2)_2$. This complex is stable to 10% NaOH , and is thermally stable at 150°C *in vacuo* over 3 weeks; at 200°C it decomposes forming methane [324].

Cleavage of the tin-platinum bond in Pt(IV) complexes has been observed [304] (eqn 7.214).



7.11 Copper, silver and gold

Tin complexes of these metals all involve the transition metal in its +1 oxidation state with coordination numbers of two, three or four. Surprisingly, in view of its general chemistry, two-coordinated copper complexes [325], (e.g.

eqn 7.215) have been described [325] together with related salts such as $\text{Li}[\text{Me}_3\text{Sn}-\text{CuSPh}]$, $\text{Li}[\text{Me}_3\text{Sn}-\text{CuCl}]$ and $\text{Li}_2[(\text{Me}_3\text{Sn})_3\text{Cu}]$ [326].

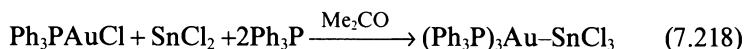
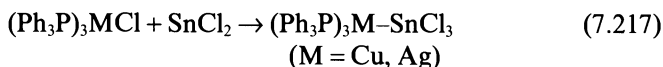


The four-coordinated complex $\text{Ph}_3\text{Sn}-\text{Cu}(\text{PPh}_3)_3$ is formed from Ph_3SnK and $\text{ClCu}(\text{PPh}_3)_3$ in benzene [327] or by reaction 7.216 [328].

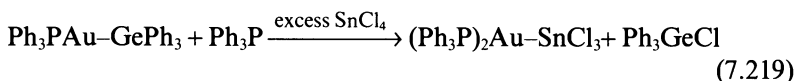


The reaction between $\text{CuBr}\cdot\text{SMe}_2$ and Me_3SnLi in THF at -78°C gives an uncharacterized complex written as $\text{Me}_3\text{SnCu}\cdot\text{LiBr}\cdot\text{SMe}_2$ [329].

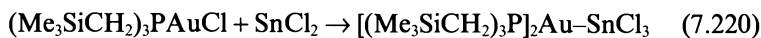
A versatile preparative method is the insertion of SnCl_2 into the $\text{M}-\text{Cl}$ bond [330, 331] (eqns 7.217 and 7.218).



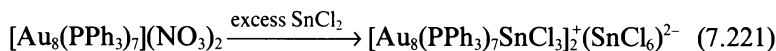
These four-coordinated complexes are white, crystalline and stable to water. The strong tendency of gold(I) to form two-coordinated complexes does not seem to apply. Heating $(\text{Ph}_3\text{P})_3\text{Au}-\text{SnCl}_3$ results in loss of 1 mol of Ph_3P , but further heating causes dissociation into Ph_3PAuCl and SnCl_2 . The action of SnCl_4 on $\text{Ph}_3\text{PAu}-\text{GePh}_3$ in the presence of Ph_3P results in reaction 7.219 [332]:



The structure of the three-coordinated complex $(\text{Me}_2\text{PhP})_2\text{Au}-\text{SnCl}_3$ suggests that it is best formulated as the salt $[(\text{Me}_2\text{PhP})_2\text{Au}]^+(\text{SnCl}_3)^-$ since the tin-gold distance is large at 288 pm; the $\text{P}-\text{Au}-\text{P}$ angle is 134° [333]. Use of the bulky phosphine $(\text{Me}_3\text{SiCH}_2)_3\text{P}$ gives the stable three-coordinated complex (eqn 7.220) [334].



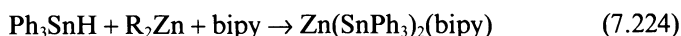
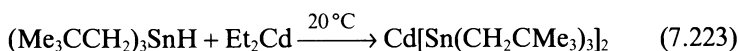
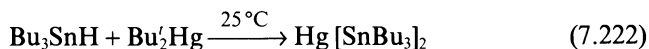
Of the Group 11 metals, gold is especially prone to form cluster complexes, and two early examples, neither of which has been characterized, have the compositions $(\text{Ph}_3\text{P})_4\text{Au}_5\text{SnCl}_3$ and $(\text{Ph}_3\text{P})_2\text{Au}_3\text{SnI}_3$ [335]. A more spectacular cluster complex has been obtained by reaction (eqn 7.221) [336].



The structure of this red crystalline complex is based on each $[\text{Au}_8(\text{PPh}_3)_7\text{SnCl}_3]^+$ unit adopting a hemispherical topology.

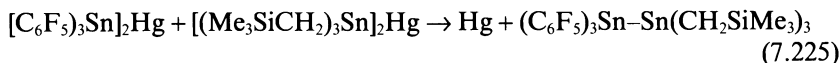
7.12 Zinc, cadmium and mercury

Organotin derivatives of all three metals have been reported. The thermal stability increases on going down the group, but all compounds are sensitive to oxygen and water. Thermal stability is enhanced by having bulky ligands which cannot undergo β -elimination of alkene (such as Me_3SiCH_2 , neopentyl) bonded to tin, or having strong Lewis bases (THF, TMED, bipy) coordinated to the otherwise vacant coordination sites on zinc, cadmium or mercury. Examples are illustrated by eqns 7.222–7.224 [337–340].



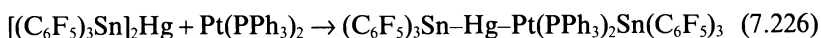
For the tin–zinc complex in the absence of Lewis bases, phenyl transfer from tin to zinc occurs. Electrochemical oxidation of zinc, cadmium and mercury in non-aqueous solutions containing Ph_3SnCl yields $\text{Ph}_3\text{Sn–MCl}$, and these compounds can be isolated if strong donors such as bipyridyl are present [341]. The reaction between Bu_3SnH , Pr^iMgCl and ZnBr_2 in ether/THF gives $(\text{Bu}_3\text{Sn})_2\text{Zn}$ and $\text{Bu}_3\text{Sn–ZnBr}$, but neither has been fully characterized [342]. Similarly, Ph_3SnH and MeCdCl form $\text{Ph}_3\text{Sn–CdCl}(\text{TMED})$ [343].

The mercury compounds $\text{Hg}[\text{Sn}(\text{C}_6\text{F}_5)_3]_2$ and $(\text{Me}_3\text{CCH}_2)_3\text{Sn–HgEt}$ [344] have been formed by the tin hydride route or, for the former compound, by irradiating a mixture of $(\text{C}_6\text{F}_5)_3\text{SnBr}$ and $(\text{Et}_3\text{Ge})_2\text{Hg}$ [345]. However, the hydride method does not always work. For example, Me_3SnH and $\text{Bu}'_2\text{Hg}$ give $\text{Bu}'_3\text{SnH}$, Me_6Sn_2 and Hg at 20°C [346]. The reaction of Me_3SnOMe with $\text{Hg}(\text{GeMe}_3)_2$ gives red crystals of $\text{Me}_3\text{Sn–Hg–GeMe}_3$ which readily decomposes into the symmetrical products [347]. Exchange reactions may also result in elimination of mercury [348] (eqn 7.225).



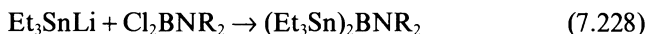
Pyrolysis or irradiation of these Sn–Hg compounds results in the formation of mercury and Sn_2R_6 [349], although more profound decomposition reactions may occur giving tin and SnR_4 [344].

The reactivity of these compounds is high and various examples have been referred to in connection with the synthesis of tin–transition metal bonds. They are highly photosensitive and react with most electrophiles and nucleophiles, often under mild conditions. Examples are I_2 , MeI [339, 340], HgX_2 , HgR_2 , Se [349] and Li [344]. $(\text{Me}_3\text{Sn})_2\text{Hg}$ is unstable even at -10°C and is hydrolysed to Me_3SnH [346]. $\text{Pt}(\text{PPh}_3)_2$ inserts into the tin–mercury bond [313], eqn 7.226.



7.13 Boron, aluminium, indium and thallium

Boron compounds have been made using standard methods [350, 351] (eqns 7.227 and 7.228).



Alternatively, $\text{Me}_n\text{Sn}(\text{BPh}_2)_{4-n}$ compounds may be formed by reacting SnCl_4 or $\text{R}_n\text{SnCl}_{4-n}$ with complexes such as $[(\text{Ph}_2\text{PCH}_2)_2\text{Co}(\text{BPh}_2)_2]$ [352].

Complexes in which tin is bonded to a polyhedral borane or carborane are of structural interest. $\text{K}[\text{B}_5\text{H}_8]$ reacts with Ph_3SnCl forming pyramidal $1\text{-Ph}_3\text{SnB}_5\text{H}_8$ [353] and the related reaction with Ph_2SnCl_2 gives $(\text{B}_5\text{H}_8)\text{Sn}(\text{Ph})_2(\text{B}_5\text{H}_8)$ as a white air-sensitive solid. Of the six linkage isomers which are possible for the latter compound, three have been isolated [354]. $1\text{-Ph}_3\text{SnB}_5\text{H}_8$ is a yellow, light- and air-sensitive solid in which tin is bonded to the apical boron $[\text{Ph}_3\text{Sn}-\text{B}(\text{B}_4\text{H}_8)]$. Under different conditions the $2,3\text{-(}\mu\text{-Ph}_3\text{Sn)B}_5\text{H}_8$ isomer can be isolated in which tin bridges two boron atoms of the cluster. The $2\text{-Ph}_3\text{SnB}_5\text{H}_8$ isomer (i.e. Sn bonded to an equatorial B) has also been identified, but not isolated [353]. The reaction between Me_3SnCl and $\text{NaB}_{10}\text{H}_{13}$ gives $\text{Me}_2\text{SnB}_{10}\text{H}_{12}$ as a crystalline solid melting at 123°C , which is fairly stable in air [355]. In this compound Me_2Sn occupies a cage position, interacting with four boron atoms; with HCl or AlCl_3 loss of Me_2SnCl_2 occurs [356]. In $[\text{Ph}_3\text{MeP}][\text{MeSnB}_{11}\text{H}_{11}]$ tin effectively completes the icosahedral structure of the anion [357].

Reaction of the carborane $[\text{nido-6,9-C}_2\text{B}_8\text{H}_{10}]^{2-}$ with SnCl_2 in THF gives, as a volatile white solid, *closo*- $1,2,3\text{-SnC}_2\text{B}_8\text{H}_{10}$ [358]. In general, these tin-boron compounds are thermally stable; the tin-boron bond is cleaved by H_2 , X_2 , sulphur and ROH .

The complex $(\text{Me}_3\text{Sn})_3\text{Al}(\text{thf})$, obtained from $(\text{Me}_3\text{Sn})_2$, mercury and aluminium, is unstable above 20°C , and the anionic complex $\text{Li}[\text{Me}_3\text{SnAlMe}_3]$, formed from Me_3SnLi and AlMe_3 , decomposed at 0°C [359]. The cubane cage structure $(\text{SnNBu}')_4$ reacts with AlCl_3 forming an adduct which contains Al-Sn bonds [360]. $\text{Bu}_3\text{Sn-AlEt}_2$, made from Bu_3SnLi and Et_2AlCl but not isolated, finds use as an organic reagent for stannylation reactions [361].

An indium-tin complex, $\text{Ph}_3\text{Sn-InX}_2(\text{tmed})$, has been isolated from the reaction between Ph_3SnX and InX/TMED ; it decomposes above 150°C [362].

Thallium-tin compounds have been made by hydrostannolysis reactions (eqns 7.229 and 7.230) [363-365].



In general these compounds are thermally unstable; reaction with Li , O_2 , Br_2 , Hg and EtOH cleaves the tin-thallium bonds.

7.14 Antimony and bismuth

Laser evaporation and photoionization of Sn/Bi has led to the identification of Sn_3Bi_4 with 22 skeleton electrons, isoelectronic with Sn_9^{4+} [366].

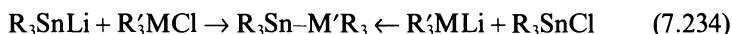
Tin–antimony and tin–bismuth bonded compounds have been little studied; they have been prepared by standard methods (eqns 7.231–7.233), bismuth compounds being the more reactive [367–369].



In the presence of AlCl_3 they decompose to SnR_4 , Sn and M. with RBr they form R_3SnBr and MR_3 [367]. On photolysis $(\text{Me}_3\text{Sn})_3\text{Sb}$ is converted into $(\text{Me}_3\text{Sn})_4\text{Sb}_2$ [370].

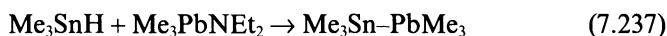
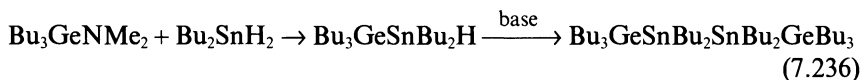
7.15 Silicon, germanium and lead

Nucleophilic substitution reactions have been applied in various ways in forming bonds to silicon, germanium and lead [371–374].



In general, these reactions give reasonable yields of the desired product, but side reactions occur due to halogen– or hydrogen–metal exchange and subsequent coupling to give the symmetrical products, R_6Sn_2 and $\text{R}'_6\text{M}_2$. A further complication is the possible dissociation of R_3SnLi to $(\text{R}_2\text{Sn})_n$ and the more strongly nucleophilic RLi . Despite these limitations this remains a good synthetic method. Other alkali metal derivatives may be used, and solvents range from ether, THF, 1,2-dimethoxyethane and HMPA to liquid ammonia.

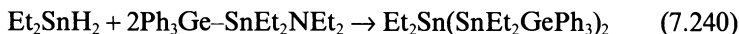
One extremely useful method of synthesis, apparently not applicable to silicon, makes use of the high reactivity of Ge–N, Sn–N or Pb–N bonds in reactions where the amine is eliminated [350, 375, 376] (eqns 7.236 and 7.237).



Synthesis by thermal or photochemical decomposition of the appropriate mercury compounds (eqns 7.238 and 7.239) has already been discussed [349].



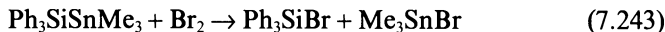
Branched chain compounds can be made by variations of these methods [376, 377] (eqns 7.240 and 7.241):



A further method of some interest is the insertion of germynes into Sn-Sn bonds [378, 379] (eqn 7.242):



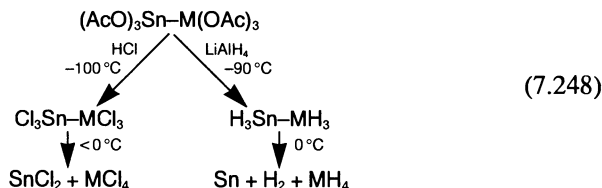
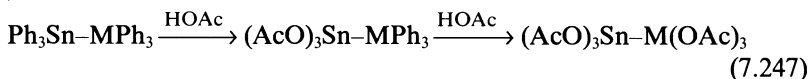
Electrophilic cleavage of the Sn-M bond (e.g. eqn 7.243) was reported as early as 1933 [380].



Nucleophilic cleavage reactions have been reported for all combinations of elements [380, 381] (eqns 7.244–7.246).



Organic, and other groups may be cleaved from either metal without breaking the Sn-M bond if reactions are carried out under sufficiently controlled conditions, as in the following sequence [382] (eqns 7.247 and 7.248).

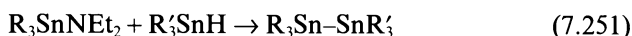


In $\text{Ph}_3\text{Sn-GeMe}_3$ the dissociation energy of the Sn-Ge bond has been reported as $297 \pm 40 \text{ kJ mol}^{-1}$ [383], and in the solid state the conformation lies between the staggered and eclipsed forms [384]. The difference in the Sn-Ge bond lengths in the isomers $\text{Ph}_3\text{Ge-SnMe}_3$ (261.1 pm) and $\text{Ph}_3\text{Sn-GeMe}_3$ (260.2 pm) reflects the relative electronic effects of Me and Ph groups bonded to Sn and Ge [385]. Predictions have been reported of π -bond strengths for currently unknown Sn=Si and Sn=Ge molecules [386].

7.16 Tin–tin bonded compounds

Aspects of the chemistry of tin cluster compounds, including zintyl anions, are discussed in Chapter 2, and the Sn–Sn bonding in stannylenes in Chapter 6.

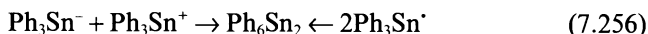
A polymeric diethyltin compound derived from EtI and Na/Sn was described in 1852 [387]. Synthetic methods for establishing tin–tin bonds have much in common with those described earlier in this section, as in the following illustrative examples [345, 349, 375, 388–390] (eqns 7.249–7.254).



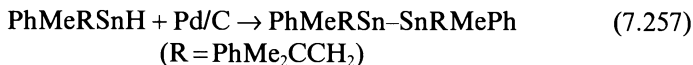
Reaction 7.254 works with dispersions of sodium, potassium and magnesium in place of titanium. Electrolytic methods involving reduction at a mercury cathode can be utilized in a number of ways, e.g. (eqn 7.255) [391].



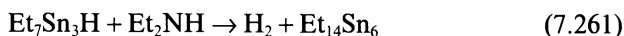
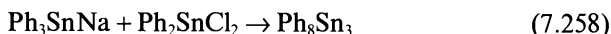
Electrochemical reduction of Ph_3SnCl in aprotic solution occurs by two different routes depending on the reduction potential [392].



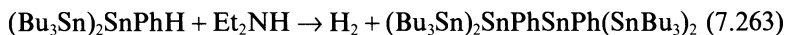
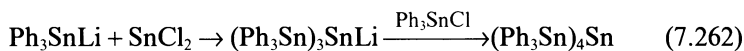
Optically active tin–tin compounds have been isolated via chiral hydrides [393] (eqn 7.257):



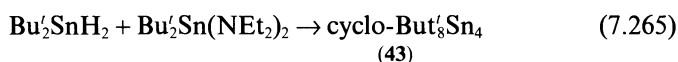
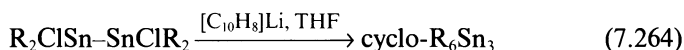
The reaction of Ph_2SnH_2 with $\text{CH}_3\text{CO}_2\text{H}$ gives $\text{Ph}_4\text{Sn}_2(\text{OCOCH}_3)_2$, in which the two acetyl groups bridge the tin atoms so that each tin is five-coordinated [394]. These methods can be extended to yield unbranched tin–tin bonded chain compounds, as in the following examples [27, 390, 395, 396] (eqns 7.258–7.261):



Further adaptations of these methods result in the formation of branched compounds [390, 397] (eqns 7.262 and 7.263).



In addition, ring systems containing between three and nine tin atoms have been prepared, usually from organotin hydrides. The size of the ring often depends on the particular experimental conditions employed, for example [398, 399] (eqns 7.264 and 7.265):



The four-membered ring in (43) is planar [400]. Other reactions leading to cyclic tetramers include the thermolysis of $\text{Bu}'_2\text{SnH}_2$ in pyridine [6] and the reaction of $\text{Bu}'_2\text{SnCl}_2$ with excess $\text{Bu}'\text{MgCl}$ in THF [401]. Cyclic pentamers are obtained from related reactions. For example, thermolysis of Ph_2SnH_2 in boiling dimethylformamide yields $\text{Ph}_{10}\text{Sn}_5$, and this reaction also gives the hexamer $\text{Ph}_{12}\text{Sn}_6$, which has a chair conformation [402]. This hexamer has also been prepared from Ph_2SnCl_2 and sodium naphthalide in THF [402]. The reaction between Me_2SnH_2 and $\text{Me}_2\text{Sn}(\text{NEt}_2)_2$, if carried out in the absence of oxygen and light, gives exclusively the hexamer $\text{Me}_{12}\text{Sn}_6$, which in solution equilibrates to include cyclomers with seven, eight and nine tin atoms in the ring [403]. Similarly, Ph_2SnH_2 and $\text{Bu}'_2\text{Hg}$ at -30°C form $\text{cyclo}-(\text{Ph}_2\text{Sn})_n$ with $n=4, 5, 6$ and 7 [346], and decomposition of Et_2SnH_2 with pyridine and Et_2SnCl_2 gives a 94% yield of $(\text{Et}_2\text{Sn})_9$ [404].

In addition to these well defined compounds, tin forms polymers of the type $(\text{R}_2\text{Sn})_n$ usually along with linear and cyclic compounds in the reactions already referred to. Chemical degradation of these polymers shows that they contain $[\text{R}_3\text{Sn}]$, $[\text{R}_2\text{Sn}]$, $[\text{RSn}]$ and $[\text{Sn}]$ units [1].

Chemical reactions of tin-tin bonded compounds mostly result in cleavage of the Sn-Sn bonds. Reversible homolytic dissociation of the Sn-Sn bond in ditin compounds occurs if bulky substituents are attached to tin, e.g. eqn 7.266.



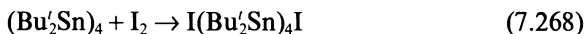
ESR signals of the radicals can be detected at elevated temperature but disappear on cooling [405]. Other ditin compounds are thermally stable to $150\text{--}200^\circ\text{C}$, the main decomposition products being R_4Sn , tin and hydrocarbons [406]. Polymeric (R_2Sn) compounds decompose to R_4Sn , R_6Sn_2 and other products [407].

In the cation Me_6Sn_2^+ , generated by radiolysis of Me_6Sn_2 at 77 K in CFCl_3 , the electron couples to the spin $\frac{1}{2}$ isotopes of tin. Analysis of the spectrum suggests that each Me_3Sn group is nearly planar, the Sn–Sn bonding MO being largely $4p_z + 4p_z$ in character [408].

R_6Sn_2 compounds react with $\text{R}\cdot$ radicals to give R_4Sn and $\text{R}_3\text{Sn}\cdot$. Reaction with oxygen occurs readily, especially for alkyls, giving $(\text{R}_3\text{Sn})_2\text{O}$ [409]. Sulphur and selenium form analogous products [410] and peroxides cleave the tin–tin bond [411] (eqn 7.267); diacetyl peroxide cleaves the tin–tin bond in a non-radical process forming $\text{R}_3\text{SnOCOCH}_3$ [412].



Electrophiles readily cleave the tin–tin bond. For iodine, kinetic studies suggest that a polar rather than a four-centred transition state is involved [413]. The product of halogen cleavage, R_3SnX , may undergo subsequent redistribution reactions, depending on the conditions used, and this consideration applies to cleavage of the tin–tin bond by SnCl_4 , organotin halides and HX [6, 406]. Cyclic tin compounds are more chemically reactive; reaction with electrophiles can be limited to ring opening [414] (eqn 7.268):



Solvolysis of Ph_6Sn_2 by RCO_2H leads to the formation of the mixed-valence complexes $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{O}(\text{O}_2\text{CR})_4\text{O}(\text{OCR})_2]_2$, in which the four tin atoms are held together by bridging carboxylate groups and two μ_3 -oxo bridges. Both Sn(IV) atoms are octahedrally coordinated, and both Sn(II) atoms have pentagonal bipyramidal geometry [415]. Me_6Sn_2 and $\text{ClCH}_2\text{CO}_2\text{H}$ react under mild conditions without cleavage of the tin–tin bond forming $\text{Me}_4\text{Sn}_2(\text{OCOCH}_2\text{Cl})_2$ with bridging chloroacetato groups [416]. HgCl_2 gives mercury and Me_3SnCl [417], and Me_3PbCl reacts in a related way forming Me_4Pb , PbCl_2 and Me_3SnCl [418]. Me_6Sn_2 and tetracyanoethylene form a charge-transfer complex, the product being the highly reactive adduct, $\text{Me}_3\text{SnC}(\text{CN})_2\text{C}(\text{CN})_2\text{SnMe}_3$ [419, 420].

Sulphur dioxide reacts with Me_6Sn_2 , forming a polymeric product by insertion into the tin–tin bond. By contrast, Ph_6Sn_2 reacts by SO_2 insertion into the Ph–Sn bonds [421]. C_2F_4 and other fluoroalkenes insert into the tin–tin bond, as do halocarbenes [422, 423] (eqns 7.269 and 7.270):

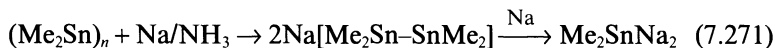


CF_3I also cleaves the tin–tin bond in Me_6Sn_2 forming Me_3SnI and Me_3SnCF_3 [424].

Addition of Me_6Sn_2 to allene is catalysed by $\text{Pt}(0)$ complexes and yields $\text{Me}_3\text{SnCH}_2\text{C}(\text{SnMe}_3)=\text{CH}_2$. Other allenes give mixtures of tin-substituted monoalkenes [425]. Diphenylethyne undergoes a similar reaction to give

trans-R₃SnC(Ph)=C(Ph)SnR₃ [426]. Oligomeric (Me₂Sn)_n compounds and (Me₂SnS)₃ combine to give Me₂SnSnMe₂SSnMe₂S [427].

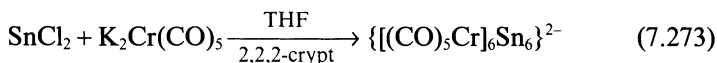
Most nucleophilic reactions have already featured in earlier sections. Ph₆Sn₂ is evidently unaffected by hot NaOH in ethanol [6]. For polymeric compounds reaction with alkali metals proceeds in stages [27] (eqn 7.271).



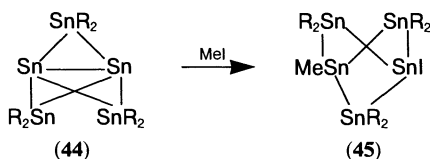
Me₃SnLi and Et₆Sn₂ undergo rapid exchange in THF [428] (eqn 7.272).



In addition to zintyl anions [429] a variety of tin cluster compounds have been isolated and their reactions examined. For example, the yellow crystalline anionic product of eqn 7.273 consists of an almost regular octahedron of tin atoms, each with an *exo*-(CO)₅Cr group bonded to it [430].



Reaction of the [1.1.1] propellane R₆Sn₅ (44) with MeI results in oxidative cleavage of the central Sn-Sn bond forming (45) [431, 432].



Thermolysis of cyclo-(R₂Sn)₃ [R=2,6-Et₂C₆H₃] in the presence of naphthalene or benzophenone yields a variety of polycyclic oligomers [R₆Sn₅ (propellane), R₈Sn₈(cubic), R₁₀Sn₁₀] in which [n]prismane structures predominate [433].

7.17 Structure and bonding

Applications of NMR and Mössbauer spectroscopy to the structure and bonding in tin compounds in general are considered in Chapters 13 and 14. Many tin-metal compounds have been examined by X-ray crystallography, and for transition metals it appears that the Sn-M bond length is significantly shorter than the sum of the covalent radii. In R₃Sn-M compounds, the Sn-M length decreases with increasing electronegativity of the R groups (Me₃Sn-M > Cl₃Sn-M for related structures) [129]. For transition metal complexes the length of the Sn-M bond increases with increasing π-acceptor properties of, in particular, the ligand *trans* to tin. No systematic changes in

Sn–M bond lengths can be correlated with changes in the formal oxidation state of the transition metal [3]. These effects can be accounted for in terms of variations in the extent of $d\pi$ – $d\pi$ interaction between tin and the transition metal. In $\text{Cl}_3\text{Sn-M}$ complexes the electronegative chlorine atoms lower the energy of the d -orbitals on tin, making them more compatible with the energies of filled d -orbitals of the transition metal. Similarly, it can be argued that, in the system *trans*- $\text{R}_3\text{Sn-M-L}$, changing L from say CO to a tertiary phosphine, which is a stronger σ -donor and a weaker π -acceptor than CO, makes a predictable change in the Sn–M bond length [$\text{Ph}_3\text{Sn-Mn(CO)}_5$, 267.4 pm; and *trans*- $\text{Ph}_3\text{SnMn(CO)}_4(\text{PPh}_3)$, 262.7 pm]. Although arguments seem reasonably self-consistent, definitive proof is lacking and bond length variations can be accounted for in terms of purely σ -bond effects based on variations in mixing of the metal bonding orbitals, a high s -character to the Sn–M bond resulting in bond shortening. This in general seems to be substantiated by NMR studies of coupling constants between tin and transition metals with a spin $\frac{1}{2}$ isotope, and between tin and hydrogen in methyltin compounds [434]. In complexes of the type $(\text{R}_3\text{P})_2\text{Pt(Ph)(SnR}_3)$, trends in Pt–P and Sn–P coupling constants lead to the conclusion that Sn–Pt bonds are predominantly σ in character [435]. In platinum, rhodium and ruthenium complexes containing more than one SnCl_3 group bonded to the transition metal, $^2J(\text{Sn-Sn})$ couplings are extremely large, especially for *trans*- $\text{Cl}_3\text{Sn-M-SnCl}_3$ [436].

In *cis*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, the platinum–tin length of 235.6 pm is shorter than in $\text{Pt}[(\text{SnCl}_3)_3]^{3-}$ (255.3 pm) and this correlates with the greater $^1J(\text{Sn-Pt})$ coupling in the former (27 640 Hz), implying a high s -character to the tin–platinum bonds [302, 435, 437]. It also appears that π -bonding is greater in four- than in five-coordinate complexes [438]. Mössbauer and photoelectron spectroscopic studies on these types of compounds have led to the conclusion that π -bonding is minimal [10, 159]. Distortion of the bond angles at tin from tetrahedral in $\text{R}_3\text{Sn-M}$ compounds correlates with Sn–M coupling constants, which in turn may be correlated with the s -character of the Sn–M bond [75]. In tin–iron complexes, both tin and iron Mössbauer spectra have been examined. For β -diketone derivatives of the type $[(\text{chelat})_2\text{Sn-Fe(CO)}_4]_2$, the quadrupole splittings confirm that tin is octahedrally coordinated and iron isomer shifts suggest that tin is a stronger σ -donor than CO or R_3P [227]. Examination of Mössbauer data for a range of $\text{Cl}_3\text{Sn-M}$ compounds suggests that the Mössbauer centre shift does not satisfactorily distinguish between the formal +2 and +4 oxidation states of tin [439]. Various other methods (^{59}Co and ^{35}Cl NQR (nuclear quadrupole resonance), ^{119}Sn γ -resonance, dipole moments, ^{59}Co wideline NMR and vibrational spectroscopy) of assessing $d\pi$ – $d\pi$ contributions to bonding in tin–cobalt complexes have been considered, with the conclusion that π -bonding is non-zero and that R_3Sn is a stronger σ -donor than Cl_3Sn [235]. Electronic and ^{31}P NMR spectra have been reported for $\text{C}_5\text{H}_5(\text{Ph}_3\text{P})\text{Ni-SnCl}_3$

and the SnPh_3 analogue; these suggest that SnCl_3 and SnPh_3 lie high in the spectrochemical series [440].

Stannylenes-transition metal bond lengths are considerably shorter than those of $\text{Sn(IV)}-\text{M}$ bonds. For example, the tin-chromium distance in $\text{R}_2\text{Sn}-\text{Cr}(\text{CO})_5$ ($\text{R}=(\text{Me}_3\text{Si})_2\text{N}$) is 256.2 pm, whereas for a range of $\text{Sn(IV)}-\text{Cr}$ complexes it is about 285 pm [106]. This change is probably due to extensive π -interaction giving double bond character to the stannylenes-Cr bond, as in carbene complexes of transition metals. In $\text{Bu}_2(\text{py})\text{Sn}-\text{Cr}(\text{CO})_5$ the Sn-Cr bond length is 265.2 pm, which may be interpreted as a decrease in π -interaction relative to the stannylenes, due to coordination of a Lewis base to tin [108, 441]. Similar correlations can be made for Pt-Sn(II) and Pt-Sn(IV) complexes [296].

In polystannanes such as $\text{Me}_2\text{Sn}(\text{SnPh}_3)_2$ and $(\text{Ph}_3\text{Sn})_4\text{Sn}$, the ^{119}Sn NMR chemical shifts are strongly influenced by chain branching and the two-bond tin-tin coupling correlates reasonably well with bond lengths and bond angles [10].

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8 Radical chemistry of tin

A.G. DAVIES

8.1 Introduction

Free radical reactions of organotin compounds, particularly those which involve intermediate neutral trialkyltin radicals, R_3Sn^\cdot , have attracted a lot of attention in recent years. The important types of homolytic reactions are

- The formation and reactions of tin-centred radicals, $R_nSnX_{3-n}^\cdot$.
- Homolytic reactions which occur at a ligand in an organotin compound.
- Bimolecular homolytic substitution at the tin centre in tin(IV) compounds R_nSnX_{4-n} .
- Electron transfer reactions to generate the radical cations, $R_nSnX_{4-n}^{+\cdot}$, or anions, $R_nSnX_{4-n}^{-\cdot}$, and the subsequent reactions of these species.

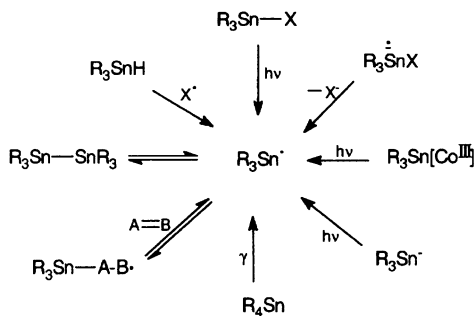
A brief review of the field was published in 1976 [1], and specific aspects, which are referred to later, have been reviewed elsewhere. A major development has involved the use of trialkyltin radicals as reactive intermediates in organic synthesis. This chemistry has been thoroughly covered in several reviews [2–7] and will not be considered in detail here. This article brings up to date the account which was published in the 1st edition of this book in 1989 [8].

8.2 Organotin radicals

8.2.1 Formation

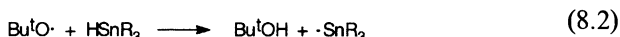
The organotin radicals are covered in the most recent volume of Gmelin [9].

The principal routes by which they can be generated are summarized in Scheme 8.1.



Scheme 8.1

From tin hydrides. For both physical studies and synthetic applications, trialkyltin hydrides provide the most common source of R_3Sn^\cdot radicals. For physical studies, the hydrogen can conveniently be abstracted by *tert*-butoxyl radicals generated by photolysis of di-*tert*-butyl peroxide. For example, if a solution of tri-*n*-butyltin hydride and di-*tert*-butyl peroxide in pentane is photolysed in the cavity of an EPR spectrometer, the spectrum of the Bu_3Sn^\cdot radical can be observed [10] (eqns 8.1 and 8.2):



If the *tert*-butoxyl radicals are generated by laser flash photolysis, the formation of the R_3Sn^\cdot radical can be monitored by optical spectroscopy to give values for the rate constants for reaction 8.2 in the narrow range of $2\text{--}4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, depending on the nature of R, at 22°C in di-*tert*-butyl peroxide as solvent [11, 12]. Alternatively, the hydrogen can be abstracted by a ketone which is photoexcited to the triplet state [13]. For example, reaction 8.3 takes place [11] with a rate constant of $2.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.



When organotin hydrides are used in organic synthesis the formation of the tin radical is usually one step in a radical chain process. The reactions may take place spontaneously, or may be initiated at or below room temperature by photolysis, by electro-oxidation [14] or by sonication [15, 16]. At $60\text{--}80^\circ\text{C}$ azoisobutyronitrile can be added as an initiator or, at lower temperature, a trialkylborane in the presence of a trace of oxygen [17], when the initiating radicals are formed by the autoxidation of the borane [18].

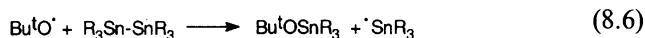
The chain carriers [4] are the organotin radical and frequently an alkyl radical R^\cdot . The propagation step which regenerates the tin radical (eqn 8.4) then has a rate constant of about $1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature, and shows an isotope effect [19, 20] of $k_H/k_D \sim 2$.



Perfluoroalkyl radicals [$k(C_7F_{15}) = 2.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$] and phenyl radicals [$k = 7.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$] [21] are much more reactive.

From distannanes. Trialkyl- or triaryltin radicals can also be formed by the homolysis of the Sn–Sn bond in a distannane (eqn 8.5). For simple hexaalkyl- or hexaarylditins, the reaction can be brought about photolytically; the quantum yield can be improved if di-*tert*-butyl peroxide is added to the system, when the bimolecular reaction (eqn 8.6) is superimposed on the unimolecular homolysis (eqn 8.5) [22]. Photolysis of cyclic oligostannanes $(R_2Sn)_n$ appears to give first the α,ω -distannyl radicals, $\cdot R_2Sn(R_2Sn)_{n-2}SnR_2^\cdot$,

which behave conventionally [23], but these systems can also serve as a source of stannylenes, R_2Sn :

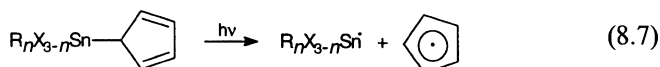


The hexaalkylditins are normally much less sensitive to homolytic attack than are the trialkyltin hydrides. Their reactions involve little chain character, and they are used more in physical studies than in organic synthesis.

If the distannanes carry bulky ligands, these can sterically weaken the Sn–Sn bond so that reversible thermal dissociation may occur without other decomposition [24]. Table 8.1 shows a correlation between the structure of the distannane and the Sn–Sn bond vibration frequency and dissociation energy, and the lowest temperature at which the EPR spectrum of the Ar_3Sn^{\cdot} radical can be detected [25, 26].

From compounds R_3SnX . Certain organotin compounds R_3Sn-X , where the Sn–X bond is weakened sterically or electronically, can similarly yield the radicals R_3Sn^{\cdot} on photolysis. Examples are given when X is NPr_2^i [27], CH_2Ph [28] and particularly when it is C_3H_5 or cobaloxime.

The ease of preparation and the general photosensitivity of the cyclopentadienyltin compounds make them convenient sources of a series of radicals with the composition $R_nSnX_{3-n}^{\cdot}$ ($X = Cl$ or C_5H_5) (eqn 8.7) [29–31] so that the effect of ligands R and X on the properties of the stannyl radicals can be studied by EPR spectroscopy.



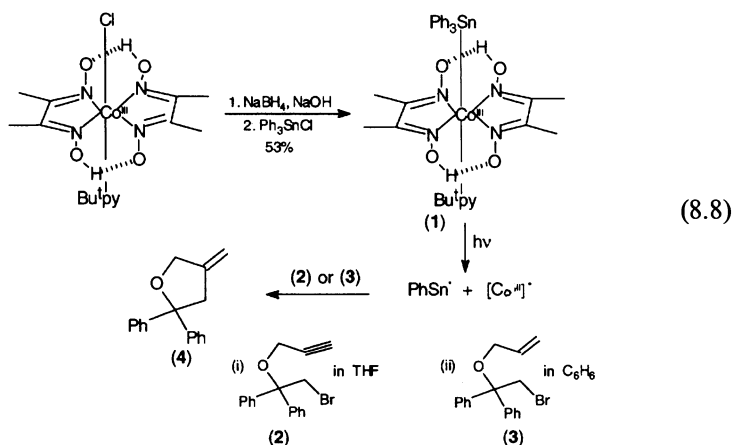
The generation of stannyl radicals from stannylcobaloximes is a new development [32], and is likely to be of more use in organic synthesis than in EPR studies. Treatment of chloro(4-*tert*-butylpyridine) cobaloxime with sodium borohydride then with triphenyltin chloride gives the stannyl-

Table 8.1 Hexaaryldistannanes $Ar_3SnSnAr_3$ in equilibrium with triarylstannyl radicals Ar_3Sn^{\cdot}

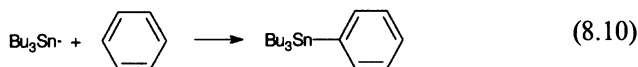
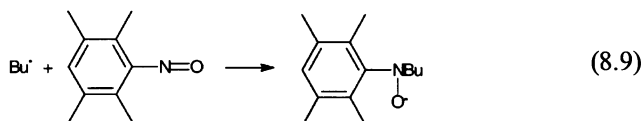
Ar	ΔH (kJ deg ⁻¹)	EPR signal (°C) ^a	<i>g</i>	$\nu(Sn-Sn)$ (cm ⁻¹)
Ph	—		2.0023	138
2-MeC ₆ H ₄	—		2.0062	125
2,3,4,5-Me ₄ C ₆ H	—		—	105
2,6-Me ₂ C ₆ H ₃	214 ± 8	170	2.0073	110
2,3,6-Me ₃ C ₆ H ₂	205 ± 8	180	2.0073	102
2,3,4,6-Me ₄ C ₆ H	184 ± 8	180	2.0064	105
2,3,4,5,6-Me ₅ C ₆	161 ± 8	130	2.0057	98
2,3,6-Et ₃ C ₆ H ₂	111 ± 8	100	2.0076	92
2,3,6-Pr ⁱ ₃ C ₆ H ₂	36 ± 4	20	2.0079	—

^aLowest temperature at which the EPR signal of the radical becomes apparent.

cobaloxime (1) (eqn 8.8). If this is irradiated with UV light in the presence of the unsaturated acyclic bromides (2) and (3), the vinylfuran (4) is formed. In the former reaction, cyclization of the alkyl radical gives a vinyl radical which abstracts hydrogen from the THF solvent; in the latter reaction, the cyclization gives an alkyl radical which presumably donates β -H to the cobaloxime radical.



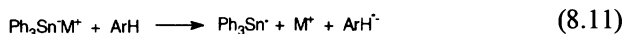
Sonolysis provides an attractive alternative to photolysis for generating stannyl radicals. Janzen has studied the ultrasonic decomposition of organotin compounds in benzene, trapping organic radicals with nitrosodurene [33]. For example, hexabutylditin in benzene yielded both butyl radicals and tributyltin radicals which were detected as shown in eqns 8.9 and 8.10:



Sonication has been shown to accelerate the reaction of triphenylstannane with alkynes by a factor of up to 600. The reactions can be carried out at temperatures down to -55°C , and they are more stereoselective [15].

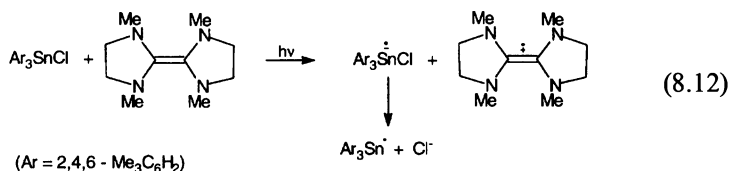
γ -Irradiation has been used for generating organotin radicals (and radical anions and cations) in either a host matrix or a self-matrix. For example, irradiation of tetramethyltin in an adamantane matrix at 77 K gave an isotropic ten-line spectrum with binomial intensity ratios [34] and EPR parameters in agreement with those obtained for the Me₃Sn[•] radical in fluid solution [35].

Electron transfer reactions. Photoinduced electron transfer from a triphenylstannyl anion to furan or methylfuran solvent, or a hydrocarbon such as anthracene, has been used to generate triphenyltin radicals (e.g. eqn 8.11) [36–38]:



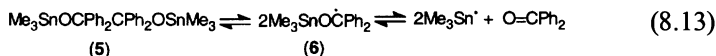
Photolysis of the stable stannylene $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}^{\cdot}$ gives rise to the radical $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}^{\cdot}$. The reaction may involve initial formation of the radicals $[(\text{Me}_3\text{Si})_2\text{CH}]\text{Sn}^{\cdot}$ and $(\text{Me}_3\text{Si})_2\text{CH}^{\cdot}$, but no evidence could be found for the addition of other radicals to the stannylenes [39, 40].

Similar radicals can be prepared by photoinduced electron transfer from an electron-rich alkene to a triaryltin chloride in toluene at low temperature (eqn 8.12) [24]. A similar electron transfer mechanism is presumably involved in the reaction of triaryltin halides with alkali metals to give the corresponding hexaarylditins.

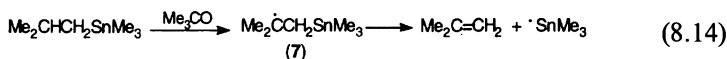


The $\text{Ph}_3\text{Sn}^{\cdot}$ radical can also be generated via the radical cation $\text{Ph}_3\text{SnH}^{\cdot+}$ by electrochemical oxidation of Ph_3SnH (section 8.5) [14].

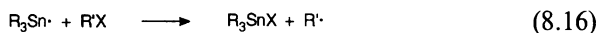
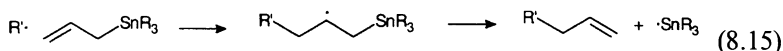
By β -scission reactions. The final route to organotin(III) radicals, listed in Scheme 8.1, involves β -scission of a radical carrying an organotin substituent at the β -position. For example, the bistrimethyltin derivative of benzpinacol (5) is in equilibrium at room temperature with the ketyl radicals (6) which at 60 °C dissociate into benzophenone and trimethyltin radicals (eqn 8.13) [41–43].



A second example of β -scission is shown in eqn 8.14 [44]. When di-*tert*-butyl peroxide is photolysed in the presence of trimethylisobutyltin, hydrogen is abstracted preferentially from the β -position of the isobutyl group, and the β -stannylalkyl radical (7) then undergoes β -scission to yield the trimethyltin radical, which can be observed by EPR spectroscopy directly, or through its reaction with ethene or an alkyl bromide.



A similar β -scission process is involved in the conjugate substitution reaction of a radical with an allylstannane.



The radical R' is frequently an organic radical derived from a compound $R'X$ where $X = \text{Cl}, \text{Br}, \text{I}, \text{SPh}, \text{SePh}, \text{OC(S)R''}$ or HgCl , when the stannyl radical which is displaced abstracts X to regenerate the radical R' and establish a chain reaction [45]. For use in organic synthesis, the reactions can be initiated with azoisobutyronitrile, or with a trialkylborane in the presence of a trace of oxygen. Similar reactions will occur where R' is a heteronuclear radical such as $\text{PhS} \cdot$, $\text{PhSe} \cdot$ or $\text{PhTe} \cdot$ (from PhSSPh , PhSeSePh or PhTeTePh , respectively), or $\text{PhSO}_2 \cdot$ (from PhSO_2Cl).

8.2.2 Physical properties

The first observations of tin-centred radicals by EPR spectroscopy were on samples in the solid state, but more recently many spectra have been recorded on fluid solutions. It is an advantage to use high microwave power, when the spectra of any interfering organic radicals are saturated, but those of the tin-centred radicals are enhanced. Spectral parameters are listed in Table 8.2 [46].

The high values of the hyperfine coupling to $^{117/119}\text{Sn}$ imply that the tin-centred radicals have a pyramidal structure (8), with the unpaired electron in an orbital with a substantial degree of σ -character and a direct interaction with the tin nucleus [34]. Application of Kaptein's rules in the ^1H CIDNP (chemically induced dynamic nuclear polarization) spectra of $\text{PhCH}_2\text{SnMe}_3$ formed from freely diffusing benzyl and trimethyltin radicals, leads to the conclusion that the sign of $a(^{117/119}\text{Sn})$ in $\text{Me}_3\text{Sn} \cdot$ is negative [51]. Radicals centred on silicon or germanium have a similar pyramidal structure (though the nature of the relationship between structure and ^{29}Si hyperfine coupling in silyl radicals has recently been questioned [52]), but carbon-centred radicals have a planar or near-planar structure (9). MNDO calculations parameterized for tin predict a similar pyramidal structure for $\text{Me}_3\text{Sn} \cdot$, and it has been suggested that the controlling factor is the σ -conjugative interactions which are greatest when the C and Sn atomic orbitals have the same sp^3 hybridization [53].

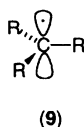
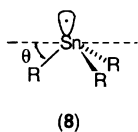
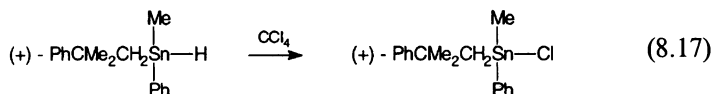


Table 8.2 EPR spectra of tin(III) radicals

Radical	<i>T</i> (K)	<i>a</i> (H or N) (mT)	<i>a</i> (¹¹⁹ Sn) (mT)	<i>g</i>	Ref.
H ₃ Sn•	4	2.6 (3H)		2.017	47
Me ₃ Sn•	193	0.31 (9H)	161.1	2.0163	10, 35
Me ₂ SnCl•	77		178	2.0113	34
MeSnCl ₂ •	77			2.0009	34, 48
Cl ₃ Sn•	77			1.9974	34
Me ₃ SnSnMe ₂ •	77	0.45 (6H)	117.1 (and 25)		48
Et ₃ Sn•	193		155	2.015	10, 48
Pr ₃ Sn•	193	0.30 (6H)	155	2.0160	10
Bu ₃ Sn•	193	0.31 (6H)	155	2.0160	10, 48
Bu ₃ Sn•	203	0.26 (3H)		2.0170	10, 44
(Me ₂ CCH ₂) ₃ Sn•	≤203	0.34 (6H)		2.0170	26
Ph ₃ Sn•	223		186.6	2.0023	10
Ph ₂ MeSn•	203	0.30 (3H)		2.0082	10
PhMe ₂ Sn•	198	0.30 (6H)		2.0124	10
PhEt ₂ Sn•	183			2.0125	10
Ph ₂ EtSn•	213			2.0072	10
(PhMe ₂ CCH ₂) ₃ Sn•	298	0.31 (6H)	138.0	2.0150	10
(Ph ₂ MeCCH ₂) ₃ Sn•	>363	0.30 (6H)		2.0145	26
(Ph ₃ CCH ₂) ₃ Sn•	418	0.33 (6H)		2.0145	26
(2,3,5-Me ₃ C ₆ H ₂) ₃ Sn•	453			2.0073	40, 49
(2,3,5-Et ₃ C ₆ H ₂) ₃ Sn•	373			2.0076	25, 49
(2,3,5-Pr ₃ C ₆ H ₂) ₃ Sn•	423		167.8	2.0078	10, 49
[(Me ₂ Si) ₂ CH] ₃ Sn•	298	0.21 (3H)	177.6	2.0094	40
[(Me ₂ Si) ₂ N] ₃ Sn•		1.09 (3N)	342.6	1.9912	40
[(Me ₂ C)(Me ₂ Si)N] ₃ Sn•		1.27 (3N)		1.9928	50
[(Me ₂ Ge) ₂ N] ₃ Sn•		1.07 (3N)		1.9924	50
[(Et ₂ Ge) ₂ N] ₃ Sn•		1.19 (3N)		1.9939	50

The ¹¹⁹Sn hyperfine coupling constants for the other radicals in Table 8.2 imply that these radicals, even when the ligands are bulky substituted aryl groups, are similarly non-planar. This structure is confirmed by the spectrum of the trineophyltin radical (PhCMe₂CH₂)₃Sn•, which shows separate coupling constants for the magnetically non-equivalent methylene protons, and an alternating linewidth effect indicating hindered rotation about the Sn–C bonds [49]. It is concluded that the radical is configurationally stable, with an angle θ of 14.0°. Again, reactions of optically active tin compounds which proceed through an intermediate tin radical can retain asymmetry at the tin (e.g. eqn 8.17) [54, 55].



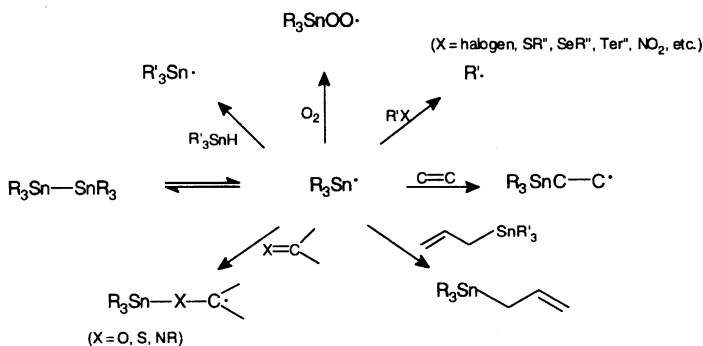
Hyperfine coupling to β-CH in the radicals (CH₃)₃M• decreases in the sequence M = C (2.27 mT) > Si (0.63 mT) > Ge (0.55 mT) > Sn (0.31 mT). Hyperfine coupling to aryl protons decreases in the same sequence: M = C [*a*(H_p) = 0.57 mT] > Si (0.12 mT) > Ge (0.093 mT) > Sn (< 0.05 mT), implying that the unpaired electron remains centred largely on the tin atom, and

this is confirmed by the similar (0.30–0.31 mT) values of $a(\text{CH}_3)$ in the radicals $\text{Me}_3\text{Sn}^\cdot$, $\text{PhMe}_2\text{Sn}^\cdot$ and $\text{Ph}_2\text{MeSn}^\cdot$. In contrast, in the radicals $\text{Me}_3\text{C}^\cdot$, $\text{PhMe}_2\text{C}^\cdot$ and $\text{Ph}_2\text{MeC}^\cdot$, the values of $a(\text{CH}_3)$ are 2.27, 1.65 and 1.56 mT, respectively.

Optical spectroscopy has been used for characterizing organotin radicals and monitoring their reactions in solution [12]. Thus the radical $\text{Bu}_3\text{Sn}^\cdot$ shows a maximum absorption at 400 nm and the radical $\text{Ph}_3\text{Sn}^\cdot$ shows a maximum at 325 nm.

8.2.3 Reactions

The principal reactions of organotin radicals are summarized in Scheme 8.2.

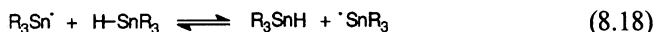


Scheme 8.2

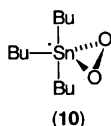
We will consider here the principles underlying these reactions, rather than their extensive applications in organic synthesis.

Self-reaction. The reversible association of sterically hindered triaryltin radicals to give hexaarylditins has been referred to above (Table 8.1). Simple trialkyltin radicals undergo self-reaction to give the corresponding ditins at rates close to those of diffusion control ($2k_1 = 1\text{--}3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [19, 35]. A ^{119}Sn CIDNP effect has been observed in the $\text{Me}_3\text{SnSnMe}_3$ which is formed by the self-reaction of trimethylstannyl radicals [51].

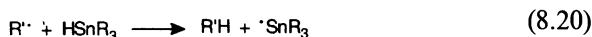
Reaction with $R_3\text{SnH}$. Simple $R_3\text{Sn}^\cdot$ radicals react rapidly with their parent hydrides by the identity reaction (eqn 8.18), which can lead to line broadening in the NMR spectrum of $R_3\text{SnH}$, and line broadening and exchange narrowing in the EPR spectrum of $R_3\text{Sn}^\cdot$, and the rate constant for reaction has been estimated [56] to be $10^6\text{--}10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The high rate of the reaction has been ascribed to the length of the Sn–H bond, which reduces the repulsion between the $R_3\text{Sn}$ groups in the transition state $[\text{R}_3\text{Sn}\cdots\text{H}\cdots\text{SnR}_3]^\ddagger$.



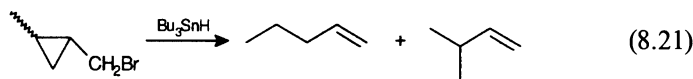
Reaction with O_2 . Triorganotin radicals react rapidly [57] with oxygen to give the corresponding peroxy radicals, $R_3SnO_2\cdot$. For $Bu_3Sn\cdot$ the rate constant is $(7.5 \pm 1.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and it has been suggested that the spin selection factor of $1/3$ for the reaction doublet + triplet \rightarrow doublet may be overcome by the effect of the heavy tin atom. Whereas *tert*-alkylperoxy radicals ($ROO\cdot$) are in equilibrium at low temperature with the corresponding tetroxides ($ROOOOR$), the stannylperoxy radicals are long-lived at low temperature. In the radicals $R_3SiOO\cdot$ and $R_3GeOO\cdot$, ^{17}O studies show that the two oxygen atoms are non-equivalent but, remarkably, the $Bu_3SnOO\cdot$ radical which is singly labelled with ^{17}O labelled ($I^{5/2}$) in either of the possible positions, ($Bu_3Sn^{16}O^{17}O\cdot$ or $Bu_3Sn^{17}O^{16}O\cdot$) shows only a single sextet with $a(^{17}O) = 2.5 \text{ mT}$, $g = 2.026$ [58, 59]. This implies that the two oxygen atoms are equivalently bound to the tin in a structure such as (10).

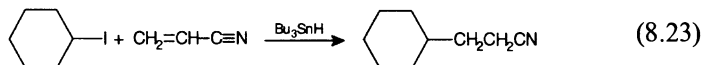
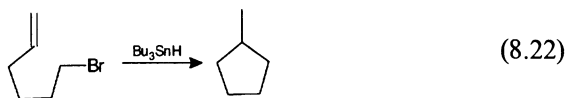


Substitution at X in RX . The observation in 1957 [60, 61] that allyl halides were reduced to propene by trialkyltin hydrides was the first example of a reaction which has since achieved great importance in synthetic and mechanistic organic chemistry. The reaction shows all the usual characteristics of a radical chain process, and is well established to involve an S_H2 reaction by a tin radical at the halogen centre to displace an organic radical (eqn 8.19), which abstracts hydrogen from the tin hydride to regenerate the tin radical (eqn 8.20) [4, 62–65].



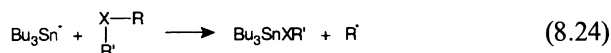
Reaction 8.20 has been discussed above. The most direct evidence for reaction 8.19 is provided by the fact that EPR spectra of the radicals $R'\cdot$ can be observed when a distannane such as hexabutylditin is photolysed in the presence of an alkyl halide (eqns 8.5 and 8.19) [22, 35, 66]. Stronger spectra are obtained when di-*tert*-butyl peroxide is present, because of the occurrence of reaction 8.6. Some typical reactions which emphasize the homolytic mechanism of these halogen abstraction reactions are shown in eqns 8.21 [66], 8.22 [67] and 8.23 [68].





Ab initio calculations indicate that reaction 8.19 involves a co-linear transition state, without the intervention of a hypervalent intermediate [69]. The presence of chloro or cyclopentadienyl ligands on the tin reduces the reactivity of the tin-centred radicals in reaction 8.19 [30, 31]. A few measurements have been made of the absolute rate constants for the halogen abstraction reaction 8.19, and of many of the relative values. A selection of the data is given in Table 8.3 [70]. Reactivity follows the sequences $\text{RCl} < \text{RBr} < \text{RI}$ and $p\text{-RX} < s\text{-RX} < t\text{-RX}$, reflecting the relative stabilities of the alkyl radicals.

Thiols and thioethers are cleaved by trialkyltin hydrides by a mechanism involving bimolecular substitution at the heteroatom X (eqn 8.24) [74, 75].



The reactivity increases in the sequence $\text{R}=\text{Me} < \text{R}^p < \text{R}^s < \text{R}' < \text{allyl}$ or *benzyl*. Selenides and tellurides are more reactive in the same sense. In contrast, ethers (or alcohols) cannot be reduced by the $\text{Bu}_3\text{Sn}^\bullet$ radical, but both peroxides and disulphides are cleaved [76, 77], the latter 10 to 100 times more readily than the former. Some rate constants are given in Table 8.4.

Addition to alkenes and alkynes. Organotin radicals add reversibly to alkenes and alkynes to give β -stannylalkyl radicals (eqn 8.25). If the source of

Table 8.3 Rate constants at *c.* 298 K for the reaction of trialkyltin radicals with alkyl halides ($\text{R}'\text{X}$)

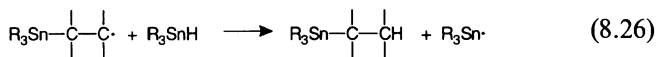
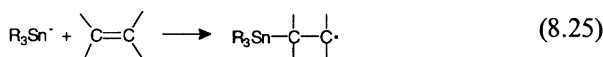
R_3Sn	R'	X	k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Ref.
$\text{Bu}_3\text{Sn}^\bullet$	Me	I	4.3×10^9	71
$\text{Bu}_3\text{Sn}^\bullet$	Pr	Br	2.6×10^7	71
$\text{Bu}_3\text{Sn}^\bullet$	Me_3C	Cl	2.7×10^4	71
$\text{Bu}_3\text{Sn}^\bullet$	Me_3C	Br	1.4×10^8	71
$\text{Bu}_3\text{Sn}^\bullet$	PhCH_2	Cl	1.1×10^6	71
$\text{Bu}_3\text{Sn}^\bullet$	PhCH_2	Br	1.5×10^9	71
$\text{Bu}_3\text{Sn}^\bullet$	$\text{Me}_3\text{SnCH}_2\text{Br}$	Br	2.11×10^8	72
$\text{Bu}_3\text{Sn}^\bullet$	$\text{Me}_3\text{Sn}(\text{CH}_2)_2\text{Br}$	Br	1.18×10^8	72
$\text{Bu}_3\text{Sn}^\bullet$	$\text{Me}_3\text{Sn}(\text{CH}_2)_3\text{Br}$	Br	3.4×10^7	72
$\text{Ph}_3\text{Sn}^\bullet$	Bu	Cl	5.2×10^2	73
$\text{Ph}_3\text{Sn}^\bullet$	Bu	Br	3.1×10^6	73
$\text{Ph}_3\text{Sn}^\bullet$	Me_3C	Cl	1.4×10^4	73
$\text{Ph}_3\text{Sn}^\bullet$	CH_2	Cl_2	3.2×10^4	73
$\text{Ph}_3\text{Sn}^\bullet$	CH	Cl_3	2.0×10^6	73
$\text{Ph}_3\text{Sn}^\bullet$	$\text{ClCH}_2\text{CH}_2\text{Cl}$		4.5×10^3	73

Table 8.4 Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for the reaction of tributyltin radicals with compounds R_2X and R_2X_2 ($\text{X}=\text{O}, \text{S}, \text{Se}, \text{Te}$)

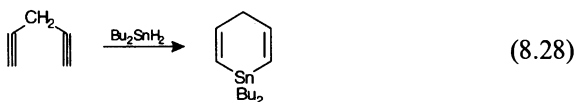
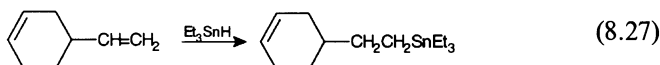
	k_2^a		k_2^b
MeSMe	<10	EtOOEt	2.5×10^4
		MeC(O)OOC(O)Me	1.4×10^5
MeSeMe	3.7×10^5	Bu'OOBu'	10^2
MeTeMe	1.4×10^7	BuSSBu	1.1×10^6
		Bu'SSBu'	7.9×10^4

^aAt 298 K in hydrocarbons.^bAt 283 K in benzene.

the tin radicals is an organotin hydride, a chain reaction is set up by reaction 8.26, leading to overall hydrostannation of the alkene or alkyne [60, 78].



The reactions may occur spontaneously or may be initiated by light, sonication [15] or electrolysis [14], by a palladium catalyst [79] or by a free radical source such as azoisobutyronitrile [80]. Examples of the synthesis of organotin compounds by hydrostannation are given in eqns 8.27 [80] and 8.28 [81].



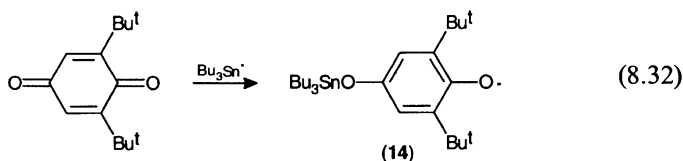
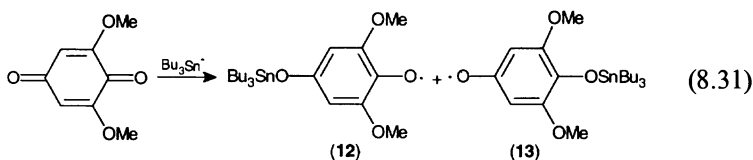
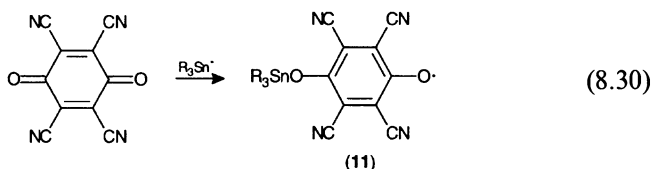
Addition to carbonyl groups. If tributyltin radicals are generated from hexabutylditin in the presence of an aldehyde or ketone (but not an ester), the EPR spectrum of the corresponding stannyloxyalkyl radical can be observed (eqn 8.29) [82].



If a tin hydride is used as the source of the tin radicals, a chain reaction is set up leading to overall hydrostannation of the carbonyl group, and trialkyltin hydrides or dialkyltin dihydrides (particularly in the presence of a small amount of dialkyltin dihalide) can be used for reducing aldehydes or ketones to alcohols [4]. The rate constants for the reaction of $\text{Bu}_3\text{Sn}^\cdot$ radicals with cyclohexanone and with 9-fluorenone have been determined by the laser flash photolysis technique to be $<5 \times 10^4$ and $(3.8 \pm 0.5) \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$, respectively, at 300 K [71]. The stannyl radicals are thus less reactive than the

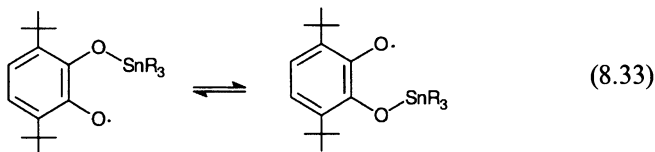
corresponding silyl radicals, but similar in reactivity to the germyl radicals.

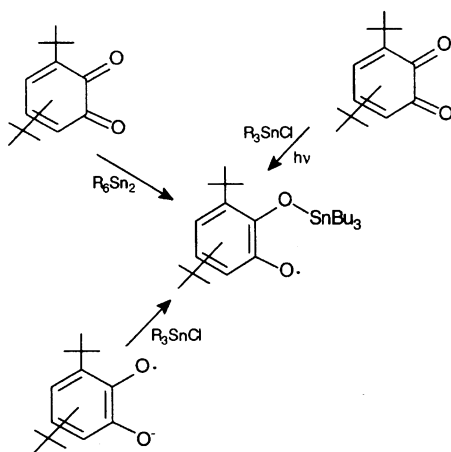
More work has been carried out on the adducts which are formed with *para*- or *ortho*-quinones, or with 1,2-diones, when the products may adopt a variety of structures [46]. The rate constant for the addition of the $\text{Bu}_3\text{Sn}^\cdot$ radical to duroquinone has been shown to be $(1.4 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [71]. Tetracyanobenzoquinone reacts with hexaalkylditins to give stable free radicals which presumably have the structure (11) ($\text{R} = \text{Me}$, Pr or Bu) [76]. 2,6-Dimethoxybenzoquinone gives a 1:5 mixture of the isomers (12) and (13) [77], but 2,6-di-*tert*-butylbenzoquinone gives only the adduct (14) [83].



A similar reaction occurs between 3,5- and 3,6-di-*tert*-butylbenzo-1,2-quinone (Scheme 8.3), and the same adducts can also be made by a variety of other processes such as the reaction of the semidione radical ion with the appropriate alkyltin halide [84, 85], or by generating the $\text{R}_3\text{Sn}^\cdot$ radical by photolysis of a cyclopentadienyltin compound [31].

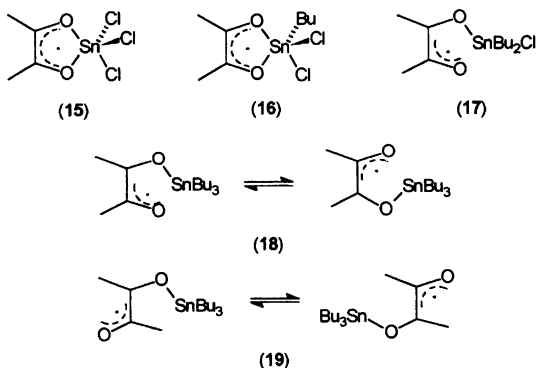
By variable-temperature EPR spectroscopy, the rate constant for the metallotropic shift (eqn 8.33) has been shown to be $c. 2.5 \times 10^6 \text{ s}^{-1}$ at 333 K when $\text{R}_3\text{Sn} = \text{Me}_2\text{SnCl}$ or Bu_2SnCl , but $> 10^9 \text{ s}^{-1}$ when $\text{R}_3\text{Sn} = \text{Me}_3\text{Sn}$ or Bu_3Sn [31, 86]. The rate constant for the corresponding shift of Me_3Si is $c. 2.5 \times 10^6 \text{ s}^{-1}$.



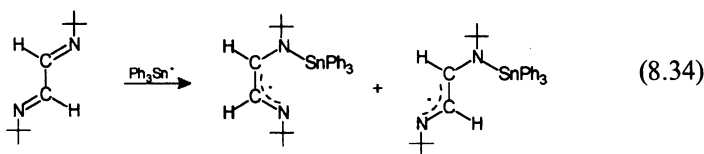


Scheme 8.3

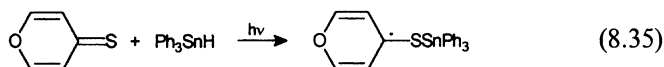
A larger variety of adduct structures can be observed with biacetyl [30]. The EPR spectra indicate that adducts formed from the $\text{Cl}_3\text{Sn}^\cdot$ and $\text{BuCl}_2\text{Sn}^\cdot$ radicals have the five-coordinate trigonal bipyramidal structures (15) and (16). The radical $\text{Bu}_2\text{ClSn}^\cdot$ forms the four-coordinated adduct (17) which is not fluxional on the EPR time scale up to 0°C , but $\text{Bu}_3\text{Sn}^\cdot$ gives the rapidly fluxional *cis* adduct (18), and the more slowly fluxional *trans* adduct (19) [30].



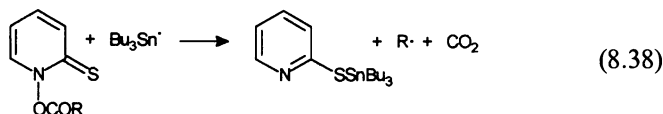
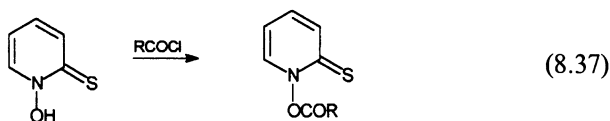
Addition to other multiple bonds. Triphenyltin radicals react with 1,4-diaza-1,3-butadienes (the nitrogen analogues of the 1,2-diones) to give rapidly fluxional *cis* and slowly fluxional *trans* adducts (eqn 8.34) [87].



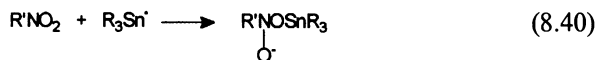
Tin-centered radicals also form adducts with thiocarbonyl compounds [11, 88, 89]. Some examples are given in equations 8.35 and 8.36:



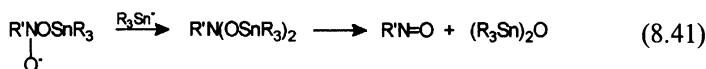
The attack of tin-centred radicals at the sulphur of a thiocarbonyl group is a component step in a number of organic synthetic procedures. An important example is the decarboxylation of a carboxylic acid as shown in eqns 8.37–8.39 [90].



Organotin radicals also form adducts with aromatic and aliphatic nitro-compounds (eqn 8.40) [31, 91], and azides are reduced to amines [92].



When $\text{R}' = \text{alkyl}$, $a(\text{N}) = c. 3 \text{ mT}$, and the radical is probably pyramidal at nitrogen, but when $\text{R}' = \text{aryl}$, $a(\text{N}) = c. 1.5 \text{ mT}$ and the structure is probably planar. With an excess of the metallating agent, these stannyloxynitroxyl radicals are reduced further to stannyloxyaminyl radicals, $\text{R}'\text{N}^\cdot\text{OSnR}_3$, probably by the reactions shown in eqns 8.41 and 8.42 [91].



When R' is a tertiary or secondary alkyl group, the stannyloxynitroxyl radicals undergo β -scission to give alkyl radicals, and tributyltin hydride in

refluxing benzene will reduce *sec*- or *tert*-alkyl compounds to the corresponding alkanes [93, 94].

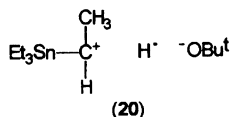


8.3 Homolytic reactions at the ligands in organotin compounds

The introduction of an R_3Sn substituent into an alkane enhances the ease of abstraction of hydrogen on the α - or β -positions by *tert*-butoxyl radicals [1, 44, 95, 96]. Relative reactivities (per hydrogen atom) are given as follows:

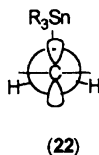
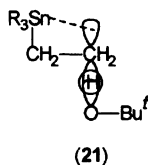


A similar but smaller effect is found for R_3Si and R_3Ge substituents. The enhanced reactivity at the α -position may be ascribed to the contribution which the polar canonical form (20) makes to the transition state, the positive charge being stabilized by inductive electron release by the Et_3Sn group.



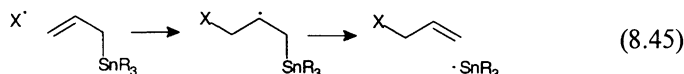
Anchimeric assistance of the abstraction of β -hydrogen implies incipient stabilization of the developing carbon radical as illustrated in (21) [96].

This interaction is apparent in the fully developed, β -trialkylstannylalkyl radicals, which have the preferred eclipsed conformation (22). This confers a low value and a positive temperature coefficient on $a(\text{H}\beta)$ (1.584 mT at 173 K for $\text{Me}_3\text{SnCH}_2\text{CH}_2\cdot$ compared with 2.471 mT for $\text{Me}_3\text{CCH}_2\text{CH}_2\cdot$) [66], and is usually ascribed to hyperconjugation involving the singly occupied $2p$ orbital and the $\text{C}\beta\text{-Sn}$ σ^* orbital, with perhaps some contribution from homoconjugation involving a vacant $5d$ orbital on tin [1, 66, 96–98].

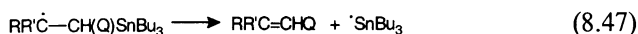
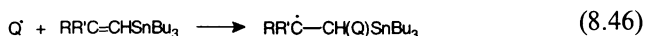


This ready formation of the β -stannylalkyl radicals, coupled with the β -scission reaction, has been exploited in the use of trimethylisobutyltin as a source of $\text{Me}_3\text{Sn}\cdot$ radicals (eqn 8.14) [44]. It is also the basis of the conjugate

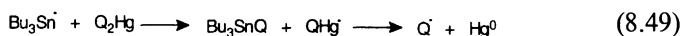
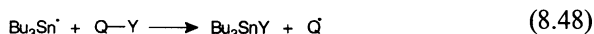
homolytic displacement (S_H2') reactions which occur with allyltin compounds (eqn 8.45) [5, 99].



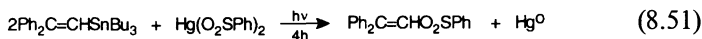
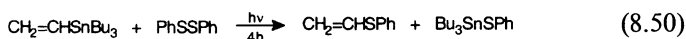
Russell [100] has shown that the radicals PhS^\cdot , RS^\cdot , PhSe^\cdot and PhSO_2^\cdot (Q^\cdot) will react with 1-alkenyl- or 1-alkynyltributyltin compounds by an addition-elimination process (eqns 8.46 and 8.47) involving the formation and fission of an intermediate β -stannylalkyl radical.



If the radical Q^\cdot is derived from a reagent QY (PhS-SPh , RS-SR , $\text{PhSe-SO}_2\text{Ar}$ or $\text{PhSO}_2\text{-Cl}$) or from a mercury(II) derivative Q_2Hg ($\text{Hg}(\text{SPh})_2$, $\text{Hg}(\text{SePh})_2$, $\text{Hg}(\text{O}_2\text{SPh})_2$ or $\text{Hg}[\text{PO}(\text{OEt})_2]_2$), the displaced $\text{Bu}_3\text{Sn}^\cdot$ radical can regenerate the radical Q^\cdot by reactions 8.48 and 8.49, and a chain reaction can be set up.

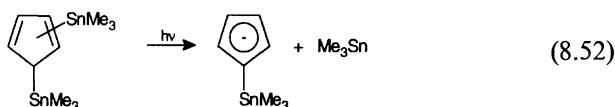


Two examples of such reactions are shown in eqns 8.50 and 8.51:

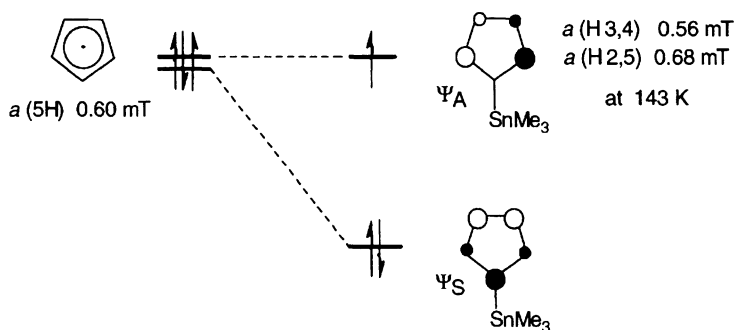


Towards the radical PhS^\cdot , $\text{PhC}\equiv\text{CSnBu}_3$ is 300 times less reactive than $\text{PhCH}=\text{CHSnBu}_3$.

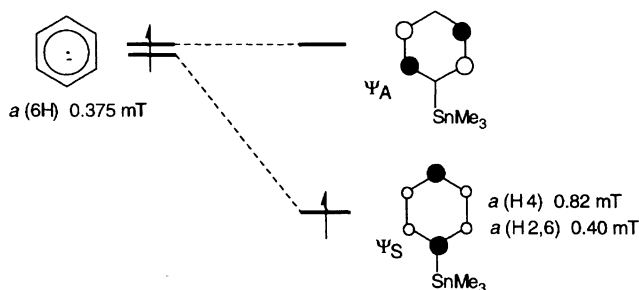
The trimethylstannylcyclopentadienyl radical has been generated by photolysis of bis(trimethylstannyl)cyclopentadiene (eqn 8.52):



The EPR spectrum shows that the Me_3Sn substituent stabilizes the ψ_s orbital so that the unpaired electron resides principally in the ψ_A orbital (Scheme 8.4) [101]. Similarly, the trimethylstannylbenzene radical anion can be generated by reduction of trimethylphenyltin, and the EPR spectrum shows that the ψ_s orbital is stabilized by the substituent (Scheme 8.5) [102].

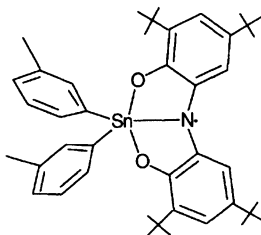


Scheme 8.4



Scheme 8.5

ortho-Aminophenols react with organotin compounds R_3SnX or R_2SnX_2 to give stable paramagnetic complexes [103]. The structure of one such complex (**23**) has been determined by single crystal X-ray diffraction [104]. The compound may be regarded as being formed by loss of a hydrogen atom from α -nitrogen, and the configuration about the tin is that of a distorted trigonal bipyramid, with equatorial aryl groups and nitrogen, and the oxygen ligands distorted away from the apical positions to give an O–Sn–O angle of 153.5° .



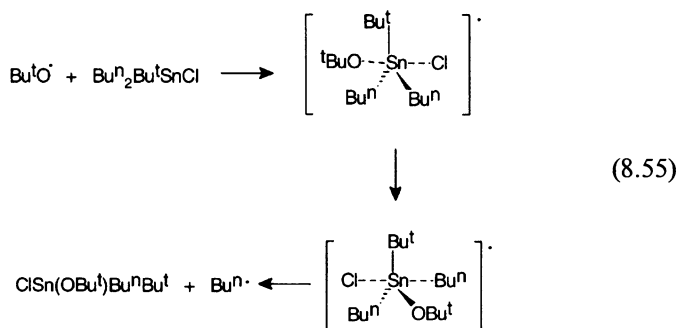
(23)

8.4 Homolytic reactions at the tin centre

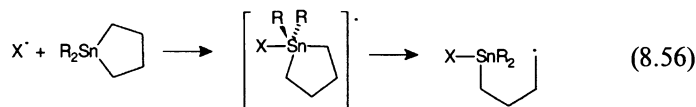
Whereas alkoxyl radicals and ketone triplets react with tetraalkyltin compounds at hydrogen centres in the alkyl groups, the presence of electro-negative ligands on the tin in compounds R_nSnX_{4-n} directs the attack to the tin centre, and an alkyl radical is displaced [1, 95, 105, 106]. Two examples are shown in eqns 8.53 and 8.54.



This change in reactivity may be associated with the greater availability of the $5d$ orbitals to form a five-coordinate transition state or intermediate, for which the structure (23) might provide a model. For the reaction of $Bu^t_2Bu^nSnCl$, EPR spectroscopy shows that the primary Bu^n rather than the more stable Bu^t radical is displaced. This may be rationalized in terms of apical cleavage in the trigonal bipyramidal transition state or intermediate where the bulky *tert*-butyl group occupies the less sterically hindered equatorial position (eqn 8.55) [107].



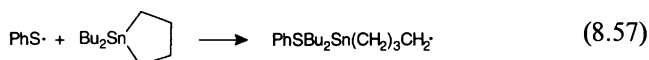
Rate constants for these reactions are collected in Table 8.5. With certain organotin compounds, or certain reagents, S_H2 reaction at tin can occur even in tetraalkyltin compounds. Thus the stannacyclopentanes show an enhanced Lewis acidity, probably because complex formation leads to relief of strain in the ring, and these compounds react with Bu^tO^\cdot , Me_3SiO^\cdot , $PhCO_2^\cdot$ and PhS^\cdot radicals with ring opening (eqn 8.56) [107].



Thiols can therefore bring about ring opening in a radical chain process as shown in eqns 8.57 and 8.58 [107].

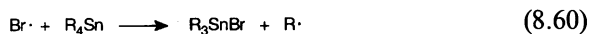
Table 8.5 Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for S_H2 reactions at tin

Reagent	$R_n\text{SnX}_{4-n}$	k	T (K)	Ref.
$\text{Bu}'\text{O}^\bullet$	Pr_3SnCl	1×10^6	283	105
	Et_2SnCl_2	1×10^6	283	105
	Bu_3SnCl	2.1×10^6	213	108
	Bu_2SnCl_2	3.0×10^6	213	108
	$\text{Bu}_2\text{Bu}'\text{SnC}$	4.5×10^6	213	108
	Me_2Sn	1.0×10^6	213	107
	Bu_2Sn	5.5×10^6	213	107
	Bu_3SnCl	4×10^8	283	105
PhMeCO^\ddagger	Bu_3SnCl	4×10^8	283	105
$(4\text{-MeC}_6\text{H}_4)\text{MeCO}^\ddagger$	Pr_3SnCl	2.2×10^8	283	105



If the alkyl groups are bulky (e.g. Bu'), or if the ring is large, some reaction also occurs at hydrogen atoms within the ring.

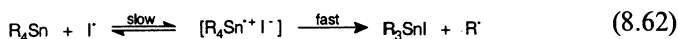
There are three important reactions in which bimolecular homolytic substitution has been suggested to occur at the tin centre in acyclic tetraalkyltin compounds. The reaction with *N*-halogenosuccinimides (eqn 8.59) follows a steric sequence in *R* [109], the reaction with bromine follows the opposite sequence (eqn 8.60) [110, 111], and the reaction with oxygen has as yet been established only where *R* = methyl (eqn 8.61) [112].



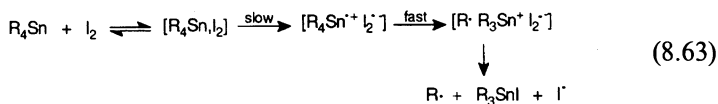
In all of these reactions, there may be some contribution of an electron transfer complex to the transition state, as discussed below.

8.5 Organotin radical ions

Fukuzumi and Kochi have shown that the selectivity (*R*/*Me*) in the reaction of photolytically generated I^\bullet atoms with organotin compounds, $\text{Me}_n\text{SnR}_{4-n}$, follows the same sequence ($\text{Bu}' > \text{Pr}^i > \text{Et} > \text{Pr}^n$) as that which is observed in the reaction of hexachloroiridate(IV), which involves an electron transfer process [113]. They suggest that the S_H2 reaction involves electron transfer to give the tetraalkyltin radical cation (eqn 8.62).



Electron transfer was also proposed to be involved in the reaction between R_4Sn and I_2 (eqn 8.63) [114].



Organotin radical cations can also be formed by thermal electron transfer from the thianthrene radical cation [115], or photoinduced electron transfer from a benzyltrialkyltin compound ($4-XC_6H_4CH_2SnR_3$; $X=Cl, F, H, Me, OMe$; $R=Me, Bu$) to methylene blue, Rose Bengal or 9,10-dicyanoanthracene (Sens). The radical cation then fragments to give the trialkyltin cation and the benzyl radical, which can initiate polymerization [116].



In other suitably substituted organotin compounds (e.g. $MeOCH_2SnBu_3$), the radical cation can fragment into the organic cation and the tin radical [117].

Flavin analogues and their Mg^{2+} complexes have similarly been used for the photosensitized formation of simple tetraalkyltin radical cations. The rates of reaction follow the sequence $Me_4Sn < Et_4Sn, Bu_4Sn < Pr_4Sn$, reflecting the relative donor ability, and the radical cations fragment to form R_3Sn^{+} and R^{\cdot} . If oxygen is present, tetramethyltin is thereby converted into the peroxide $Me_3SnOOMe$ by reaction 8.61 [112].

Radical cations can also be generated electrochemically. Electrochemical oxidation in THF of Ph_3SnH in the presence of tetrabutylammonium perchlorate gives Ph_3SnH^{+} which dissociates into H^{+} and Ph_3Sn^{\cdot} , and the latter can initiate, in good yield and under ambient conditions, the usual reactions of a stannyl radical [14].

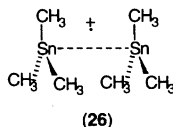
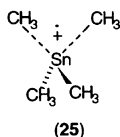
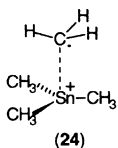
The most direct evidence for the formation of organotin(IV) radical cations comes from EPR studies of the γ -radiolysis of solid solutions in Freon matrices [118, 119]. Spectral data are listed in Table 8.6.

In Me_4Sn^{+} the hyperfine coupling to tin is small and there is a unique methyl ligand. The Me_3Sn unit is almost planar, and the bond to the remaining methyl group is elongated and weakened, as shown in the C_{3v} structure (24). Similar spectra however have been interpreted to imply hyperfine coupling to six equivalent protons, and the C_{2v} structure (25). The compounds Me_3SnR ($R=Et$ and Pr^i) showed only the spectrum of the radical R^{\cdot} , but when $R=Bu^i$, the radical cation was observed with a structure similar to (24). The C_{3v} structure is supported by PM3 calculations [121]. The low value of $a(^{119}Sn)$ in Me_6Sn_2 similarly implies that the Me_3Sn units are nearly planar, as shown in (26).

Calculations by the UHF-MNDO method are broadly in accord with these results, except that they find the Me_3Sn groups in $Me_6Sn_2^{+}$ to be non-planar [122, 123].

Table 8.6 EPR spectra of tin radical cations

Radical	Structure	Nucleus	A_{\perp} (mT)	A_{\parallel} (mT)	Ref.
SnH_4^{++}	C_{2v}	^{119}Sn	-237	-310	118
		2H	8.5	8.5	
SnH_4^{++}	C_{3v}	^{119}Sn	-318	-365	118
		1H	17.5	17.5	
MeSnH_2^{++}	C_{2v}	^{119}Sn	-238	-315	118
		2H	8.5	8.5	
$\text{Me}_2\text{SnH}_4^{++}$	C_{2v}	^{119}Sn	-238	-322	118
		2H	-8.5	8.5	
$\text{Me}_3\text{SnH}^{++}$	C_{2v} or C_{3v}	^{119}Sn	-167	-242	118
$\text{Me}_4\text{Sn}^{++}$	C_{3v}	^{119}Sn	-7.8	-21	118
		3H	1.35	-1.35	
		^{13}C	5.3	12	
$\text{Me}_4\text{Sn}^{++}$	C_{2v}	^{119}Sn	-13.3	-15.0	120
		6H	-13.8	-13.8	
$\text{Me}_3\text{SnCMe}_3^{++}$	C_{3v}	^{119}Sn	8.8		119
		9H	0.76		
		^{13}C	18.7		
$\text{Me}_3\text{SnSnMe}_3^{++}$		^{119}Sn	11.5		118-120



The observation of the EPR spectrum of the radical anion Me_3SnPh^- has been referred to earlier [102]. Photoelectron spectroscopy confirms that the first ionization potential of 1,4-bis(trimethylstannyl)benzene (8.5 eV) is less than that of benzene (9.25 eV) [124]. The EPR spectrum of the radical anion of 1,4-bis(trimethylstannyl)naphthalene has also been studied. The ^1H and ^{119}Sn hyperfine coupling constants (mT) are shown in (27) [127].

The radical anions of the methylstannanes, $\text{Me}_n\text{SnH}_{4-n}^-$, have been generated by γ -irradiation of frozen matrices such as tetramethylsilane. Data on the EPR spectra are given in Table 8.7 [125-127]. It is concluded that all these radical anions have a trigonal bipyramidal configuration, with the unpaired electron acting as an equatorial 'phantom ligand' and the methyl groups preferring to occupy an equatorial position. This is illustrated for $\text{Me}_2\text{SnH}_2^-$ in (28).

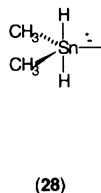
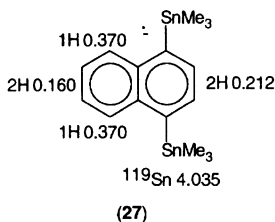
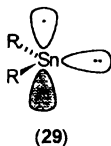


Table 8.7 EPR spectra of tin radical anions

Radical	<i>T</i> (K)	<i>g</i> _⊥	<i>g</i> _{iso}	<i>g</i>	Nucleus	<i>A</i> _⊥ (mT)	<i>A</i> (mT)	Ref.
SnH ₄ ^{•-}	77	2.000		2.010	2H _{ax}	13.8	13.7	125
					2H _{eq}	0.77	0.77	
SnH ₄ ^{•-}	100		2.00037		2H _{ax}	<i>a</i> = 14.35		126
					2H _{eq}	<i>a</i> = 0.80		
					¹¹⁷ Sn	<i>a</i> = 212.9		
MeSnH ₃ ^{•-}	77	1.997		2.012	2H _{ax}	13.2	13.1	125
	103				2H _{eq}	<i>a</i> = 0.80		
Me ₂ SnH ₂ ^{•-}	77	1.996		2.014	2H _{ax}	12.7	12.6	125
Me ₃ SnH ^{•-}	77	1.995		2.014	2H _{ax}	14.0	13.9	125
Me ₄ Sn ^{•-}	77		2.0		Sn	210.1	167.2	127

Two radical anions derived from organotin(II) compounds have been reported. Reduction of cyclo-[(2,5-Et₂C₆H₃)₂Sn]₃ with potassium amalgam in the presence of a cryptand gave rise to an ESR singlet with *g* = 2.024, and the intensity of the ^{117/119}Sn satellites, *a*(^{117/119}Sn) = 15.2 mT, indicated that this was due to the monomeric species (2,5-Et₂C₆H₃)₂Sn^{•-} [128]. Similarly, reduction of the stable stannylene [(Me₃Si)₂CH]₂Sn: with sodium in THF at -80 °C for 5–10 s gave rise to a spectrum showing a single broad line with *g* = 2.0177 and *a*(^{117/119}Sn) = 11.6 mT, which was ascribed to the radical anion [(Me₃Si)₂CH]₂Sn^{•-} [129].

The low value of the ^{117/119}Sn hyperfine coupling compared with that in the (σ) stannyl radicals R₃Sn[•] indicates that the radical anions have a π-configuration as shown in (29).



No radical cation derived from an organotin(II) compound has yet been reported.

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9 The uses of organotin compounds in organic synthesis

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The application of organotins in organic synthesis has become a major field of organometallic chemistry during the last decade. The incredible development and sophistication of known basic chemistry now allows organotins to be essential tools for the organic chemist, very often used in the preparation of natural products.

The synthesis of more and more complex molecules needs progressively more selective reagents to afford chemo-, regio- and stereoselective carbon-carbon bond formation and functional group transformations. Among organometallic reagents, organotins occupy a special place; the nature of tin-hydrogen, tin-oxygen and tin-carbon bonds, strong enough to provide stable reagents but labile enough to allow high reactivity in mild conditions, providing valuable and versatile use in organic chemistry. A sign of this popularity could be the number of syntheses involving organotins reported recently in *Organic Syntheses*: none in Collective Volume VI [1], one in Collective Volume VI [2] and seven in Collective Volume VIII [3].

The aim of this chapter, which covers the literature from 1987 up to the beginning of 1996, is not to give an exhaustive report of the applications of organotins in organic chemistry during the period (a whole book would be necessary) but to focus on the more important features. The topic has partly been discussed [4-7] and more specialized reviews are indexed under the specific headings.

9.1 Applications of tin-hydrogen bonded compounds

Organotin hydrides certainly remain the most widely used tin reagents in organic synthesis [8]. They have become textbook reagents and are universally used for two types of purposes:

- reduction of various kinds of functional groups (although most often organic halides and hydroxylated compounds);
- generation of free radicals, especially for the study of their rearrangements, which sometimes allow spectacular synthetic transformations [9-13].

It is not our aim to cover all the reactions employing tin hydrides developed in recent years but instead to show new advances and methodologies, while providing meaningful references for those who would like to study details more deeply.

9.1.1 *New hydrostannation reagents and techniques*

Although not an organotin hydride, stannane, SnH_4 , has been used for the reduction of carbonyl or nitro compounds [14]. Trineophyltin hydride gives chemo- and diastereoselective reduction of dihalopenicillanates [15] and its deuterated analog allows selective labeling [16]. Mixed (–)-menthyl-neopentyltin hydrides have been employed but with moderate enantioselectivity in the reduction of ketones [17].

It is possible to use Bu_3SnH in aqueous medium, sometimes in the presence of a detergent [18], but water-soluble oxygen-containing hydrides have been claimed to facilitate the recovery of organic products [19–21]. A nitrogen-containing stannane, more polar than the conventional ones, allows easy work-up [22] while internal nitrogen coordination to tin was shown to enhance the reducing ability [23]. Recently an easily made soluble organotin catalyst, used in aqueous base with NaBH_4 with a water-soluble radical initiator, has been employed as an *in situ* source of tin hydride [24]. A very recent proposal involves tris[2-(perfluorohexyl)ethyl]tin hydride, non-miscible in water and the usual organic solvents, which is used in homogeneous solution in trifluoromethylbenzene, all tin-containing species being removed by liquid–liquid extraction with perfluoromethylcyclohexane [25].

Ferrocenyltin hydrides [26] and vinyltin hydrides [27] have been employed and Davies has published interesting new data with mixed hydrides, Bu_2SnHX (X =halide, carboxylate, sulfenate), which appear highly reactive and allow easy recovery of tin residues, after hydrolysis, as insoluble Bu_2SnO [28]. Different methods can be employed to activate the Sn-H bond and modify its selectivity. To the classical (AIBN or irradiation) initiation of free radical processes has been added the use of Et_3B , in the presence of traces of oxygen, a system which can be employed at low temperatures [29, 30]. According to non-radical processes, Pd complexes are able to catalyze stereospecific reductions of alkenyl halides [31]. Sonication is also used to activate R_3SnH reductions at low temperatures [32] even if Et_3B is superior for the diastereoselective reduction of ribonucleosides [33]. Other means include microwaves [34], electricity [35] or high pressure [36]. Bis(tributyltin)-benzopinacolate is a new source, less toxic than the analogous trimethyltin derivative, for the thermal production of tributyltin radicals which generate processes such as reductive alkylation [37] or intramolecular cyclization [38].

The difficulty in removing traces of toxic organotin residues and the interest in recyclable reagents has placed a new emphasis on polymer-supported reagents, although non-organotin alternatives have also been proposed [39]. Neumann has demonstrated the great interest of polystyrene-bound organotin compounds, especially the tin hydride [40, 41], while similar reagents were shown to induce very low levels of organometallic pollution [42, 43].

Finally, it is worth mentioning that several systems have been described in

which a tin-containing polymeric material is used as a catalyst in the reduction of organic halides with sodium borohydride, in conditions where the actual reducing agent is a polymer-bound organotin hydride formed *in situ* [44–46].

9.1.2 Reductions through hydrostannolysis

The general scheme for the reductive process can be written as follows:

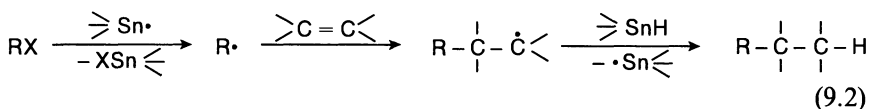


Obviously, deuterium or tritium labeling can be performed by use of the corresponding deuteride or tritide. In general, the reaction involves a homolytic process in which a tin radical $\equiv\text{Sn}^\bullet$ abstracts the atom X and gives the radical Y^\bullet which undergoes hydrogen transfer from the hydride to give the reduced product HY. Obviously, the most important case is reduction of the carbon–halogen bond but other types of bonds can also be efficiently cleaved.

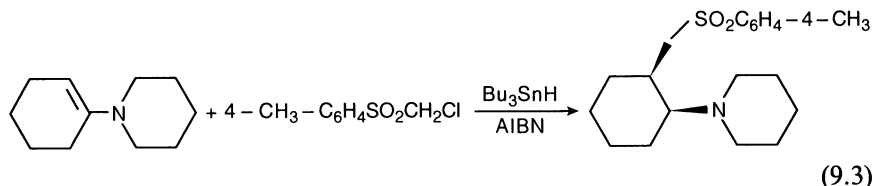
Simple reduction of carbon–halogen bonds. The tin hydride reduction is now a well established method which is used in a number of synthetic schemes [8]. Only somewhat unusual new results dealing with chemo-, regio- and stereoselectivity will be reported here. For instance, although nitro compounds are easily reduced, geminated halo-nitro derivatives are selectively dehalogenated by Bu_3SnH , even in the case of a chlorine atom [47]. Stereochemical and conformational explanations for the stereoselective dehalogenation of 2-halo sugar derivatives [48] or 2'-halo ribonucleosides [33] have been discussed. However, most of the studies have been devoted to conformational and substituent effects in stereoselective hydrogen transfer to acyclic radicals [49–52]. Some enantioselective reductions using chiral inductors or catalysts have been also reported [53, 54].

An interesting stereochemistry has been found with alkenyl halides: while (*Z*) or (*E*)-iodovinyl derivatives are non-stereospecifically dehalogenated by $\text{Bu}_3\text{SnH-Et}_3\text{B}$ [55], the process catalyzed by $\text{Pd(PPh}_3)_4$ appears to be a fully stereospecific retention of configuration. The mechanism involves insertion of Pd(0) into the carbon–halogen bond, followed by reduction and reductive elimination [31].

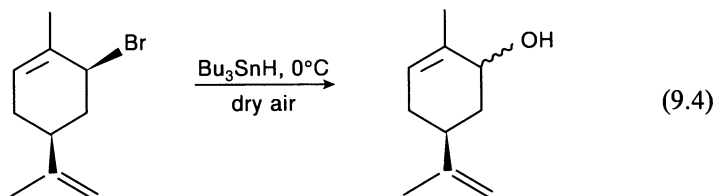
Reduction of carbon–halogen bonds with intermolecular trapping of radicals. The organic radical R^\bullet obtained from RX in the halogen abstraction step can react intermolecularly before the hydrogen transfer. Most trappings are made with alkenes, a method popularized by Giese (the intramolecular trapping will be presented in section 9.14).



Most cases involve the trapping of nucleophilic radicals with electron deficient olefins such as in the synthesis of higher carbon sugars by Bu_3SnH –AIBN reduction of iodo-sugars in the presence of alkenes [56], or the addition of homoenolic radicals derived from propionic acid (a case where the catalytic stannyl radical is produced from Bu_3SnH , formed *in situ*, by using catalytic amounts of Bu_3SnCl with NaBH_4) [57]. β -Acylvinyl radicals have been also added to electrophilic alkenes [58]. This type of reaction has been successfully included in multistep synthesis [59] while various stereochemical aspects have been described [60–63] including yield enhancement and control of diastereoselectivity by Lewis acids [64, 65]. The Giese reaction can be performed with polymer-supported organotin reagents [66]. In an interesting variant, electrophilic radicals are trapped with electron-rich olefins. Thus sulfinylated and sulfonylated carbon-centered radicals add to alkenes, enol ethers [67] and enamines [68], in this case with moderate to high stereoselectivity:



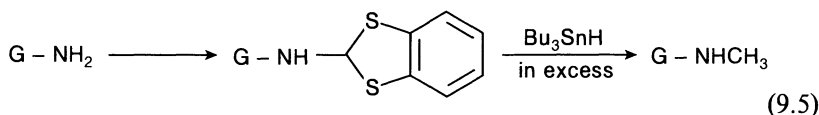
Related to the reductive alkylation, the trapping of radical R^\cdot with the $\text{C}=\text{N}$ bond of oxime derivatives has provided a good entry to dinucleosides [69]. An example of trapping by homolytic heteroaromatic substitution has also been described [70]. Reductive coupling with diazonium ions has been presented, in carbohydrate chemistry, as a synthetic route to 2-amino-2-deoxyglycosides [71]. Several examples of the synthesis of aldehydes via free radical carbonylation in the presence of carbon monoxide have appeared [72, 73]. Carbonylative cyclization leading to cyclopentanes is also possible [74], as well as double alkylation giving unsymmetrical ketones from $\text{RX-CO-Bu}_3\text{SnH}$, in the presence of an electrophilic alkene [75]. Finally, aerobic conversion of organic halides to alcohols is obtained in the presence of air, as in the following case [76, 77]:



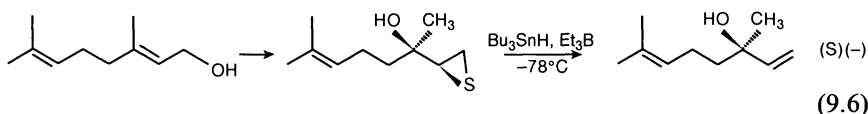
Reduction of carbon–sulfur bonds. Some new cases of $\text{S-C } sp^3$ bond cleavage have been used for specific purposes such as the desulfurization of perfluoro-

alkylated dithioketals to give perfluoroalkyl aromatics [78], 1,3-dithianes, oxathiolanes and thiazolidines [79], carbohydrate dithioketals [80] or mixed *O,S*-ketals at the anomeric position [81]. Also, a stereoselective synthesis of aryl 2-deoxy- β -glycosides has involved addition of PhSCl to glycal, Mitsunobu reaction and removal of the thiophenyl moiety by Bu_3SnH [82]. An impressive case has been reported by Boger who, in a multistep synthesis, selectively desulfurized a very highly functionalized molecule [83].

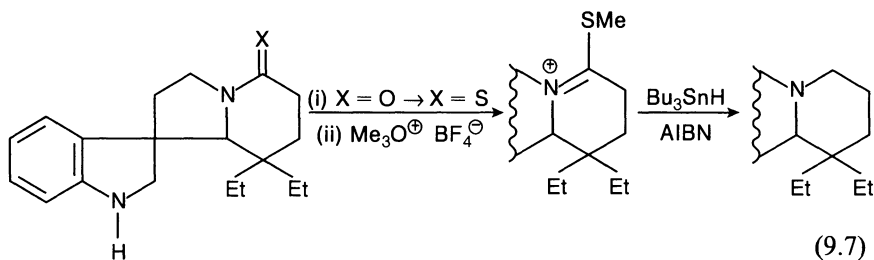
A convenient method for *N*-methylating guanosines, represented as $\text{G}-\text{NH}_2$, has been proposed via S-C bond cleavage [84].



The process can be duplicated for obtaining *N,N*-dimethyl guanosine from the *N*-methyl analog. When the sulfur atom belongs to a cycle, the desulfurization process ends up with acyclic compounds. For instance, thiiranes are transformed into alkenes with Bu_3SnH -AIBN [85] and α -hydroxy thiiranes undergo mild desulfurization to allylic alcohols with Bu_3SnH - Et_3B , a reaction nicely exemplified by the stereospecific preparation of both enantiomers of linalool from geraniol [86].



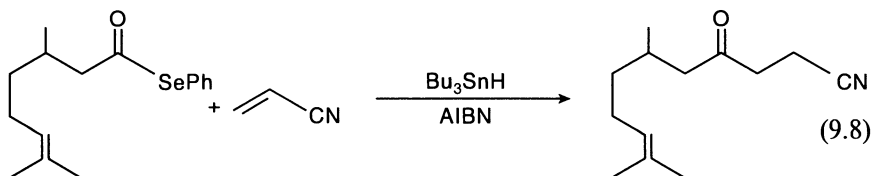
Finally the sulfur-containing five-membered ring of penicillin can be opened to dithioazetidinones by reaction with Ph_3SnH [87]. Also, the intermediate radicals can be intermolecularly trapped by alkenes [88]. In the case of S-C sp^2 bonds the situation is more complex. Vinyl sulfides react differently, the SPh group at the double bond being substituted by a tributylstannyl group, a process with synthetic interest following electrophilic cleavage of the new Sn-C bond [89, 90]. On another hand, thioesters, RCOSR' , can be reduced to aldehydes with Bu_3SnH in the presence of Pd catalysts [91] and an interesting transformation of lactams into tertiary amines, via thiolactams, should also be mentioned [92].



Several cases of reductive desulfonylation of sulfones, $\text{RSO}_2\text{Ph} \rightarrow \text{RH}$, have been described, for instance in the preparation of butyrolactones [93], disubstituted cyclopentenones such as *cis*-jasnone [94] or for the reductive desulfonylation of highly functionalized β -keto phenyl sulfones [95, 96]. Here again, it appears that vinylic phenyl sulfones undergo displacement of the sulfone by a Bu_3Sn group, a process used to obtain (*E*) and (*Z*)-terminal fluoroolefins after protodestannylation [97]. Finally, *O*-alkyl benzene-sulfonates are cleaved by $\text{Bu}_3\text{Sn}^\cdot$ to give alkoxyl radicals which can react by cyclization or β -scission [98].

Reduction of carbon-selenium and carbon-tellurium bonds. It is possible to reduce selectively one of the two Se-C bonds in 1,1-bis(organoseleno)cyclohexanes [99], an acyl C-Se bond in the presence of a vinyl C-Se bond [100] and also a Se-C bond in a sulfoxide [101]. However, more general synthetic uses have appeared, such as the transformation of RCO_2H into the corresponding isocyanide RNC via a sequence involving initial transformation into acyl azide, Schmidt rearrangement to isocyanate, addition of PhSeH to give the selenocarbamate, RNHCOSePh , and cleavage (Bu_3SnH , AIBN) to give the formamide RNHCOH , which easily dehydrated to give the target isocyanide [102].

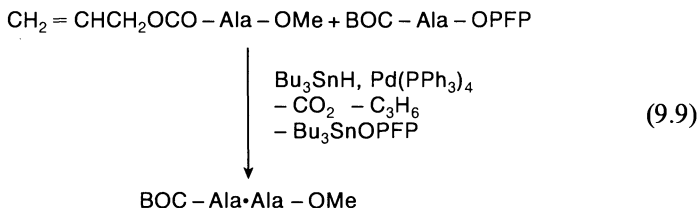
Acyl radicals, RCO^\cdot , obtained from phenyl selenoesters, RCOSePh , enter into intermolecular alkene addition reactions, although cases of intramolecular trapping have also been reported [103].



The Te-C bond in tellurolactones and telluroethers is also cleaved in high yield, while the intermediate radicals can be trapped with electron-deficient alkenes [104].

Reduction of carbon-oxygen bonds. Only in special circumstances can acyclic C-O bonds be cleaved. Examples include reduction of fullerols to fullerenes [105], trimethylsilyl triflate promoted reduction of acyclic acetals to ethers [106] and substitution of acyloxy groups in carbohydrate α -ketoesters [107]. However, under Pd catalysis, propargyl alcohols can be quantitatively deprotected from their carboxylates, phosphates, carbonates or carbamates [108]. More interesting is the deprotection of the allyl or allyloxycarbonyl group [109, 110] which can be used in the solid phase synthesis of protected peptides fragments [111, 112] or glycosylated aminoacids [113] anchored by an allylic group. Similarly, allyloxycarbonyl-protected hydrazines have been deprotected by

Bu_3SnH in the presence of Pd complexes [114]. The deprotection of *N*-allyloxy aminoacids has been extended to the *trans*-protection with an activated acyl derivative, an efficient one-pot access to amides and dipeptides [115].



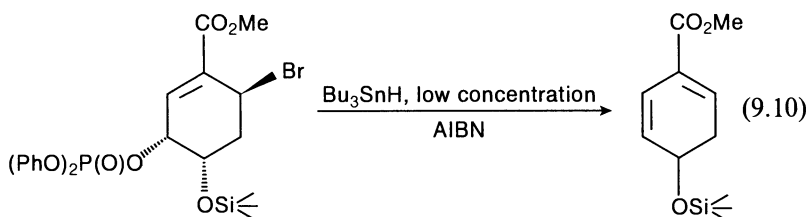
Of course, C–O bonds in oxiranes are much more reactive. While epoxides can be reduced by tin hydrides in the presence of iodide salts such as NaI or MgI_2 (in fact the iodide opens the ring and the hydride reduces the resulting iodohydrine) [116], free radical direct openings have also been observed, via initial formation of a Sn–O bond, in the case of the reduction of allylic epoxides to homoallylic [117] or allylic alcohols [118].

Reduction of carbon–nitrogen bonds. Aromatic Mannich bases of the type ArCH_2NR_2 and their derivatives (quaternary ammonium salts and amine oxides or N-oxides) have been deaminated by Bu_3SnH at *c.* 200 °C, with cleavage of the C–N bond to give ArCH_3 [119]. However, most cases deal with denitration, the reductive cleavage of C–NO₂ to C–H bonds, which has been, for instance, employed in the synthesis of alkyl fluorides [120]. In fact, this cleavage cannot be really classified as hydrostannolysis of RNO_2 since it begins with the addition of the tin radical on the N=O bond (to give a tributylstannyloxy-substituted nitroxyl radical [121, 122] which undergoes fragmentation). In a similar way the reduction of isocyanides $\text{RN}=\text{C}$ to RH , already discovered by Barton, has been successfully applied in the carbohydrate series [123].

Reduction of heteroatom–heteroatom bonds. Phosphorus–sulfur bonds have been transformed into P–H bonds with organotin hydrides [124, 125] but the more useful cleavages, in terms of organic synthesis, involve N–S bonds. Thus, sulfenamides, PhSNRR' , are a source of aminyl radicals, 'NRR'', which can lead to amines, HNRR' [126], but also undergo a number of useful rearrangements which will be described below. N–O bonds in nitrate esters, RONO_2 , lead to oxygen-centered radicals, RO' , which can be trapped by Bu_3SnH to give alcohols, ROH [127].

Reduction of carbon–carbon bonds. This reaction can only occur in special cases such as geminal dinitriles which can be transformed into mononitriles, in high yields, by a free radical process, while conventional reagents only perform total decyanation [128, 129].

Hydrostannolysis followed by elimination or fragmentation. The radicals obtained after dehalogenation of RX by an organotin radical may undergo 1,2-elimination if a suitable leaving group is present. Some cases have been observed in reductions of 1,2-acyloxy halides [130] and 1,2-halothioesters or thiocarbamates [131, 132]. An original case of 1,4-elimination is worth mentioning [133]:



1,2-Nitroalkenes, $RCH=CHNO_2$ have been transformed into *anti* γ -(phenylthio) β -nitroalcohols, $RCH(SPh)CH(NO_2)CH_2OH$, which react with Bu_3SnH by 1,2-stereoselective elimination to give (*E*)-allylic alcohols, $RCH=CHCH_2OH$ [134].

A C–C bond cleavage, following a chlorine abstraction by Bu_3Sn^\cdot in a tricyclo[5.2.1.0^{2,6}] decane skeleton, has been involved in a route to a bridged eight-membered ring related to taxane [135]. Strain and CO_2Me stabilization of the radical formed by C–C fragmentation can explain this behavior.

An indirect method to deaminate aliphatic primary amines RNH_2 involves their initial transformation into imidoyl chlorides, $R'CCl=NR$, and treatment with Bu_3SnH –AIBN to give RH via an intermediate radical $R'C^\cdot=NR$, which fragments to $R'CN$ and R^\cdot [136].

We have already seen that N–S bonds are cleaved to give aminyl radicals. They can undergo fragmentation processes as well as cyclization or ring opening [137].

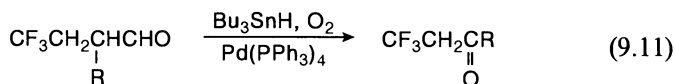
Other cases of fragmentation, followed by transpositions, will be presented in section 9.1.4.

9.1.3 Reductions through hydrostannation

Reduction of carbon–oxygen double bonds. The free radical mechanism of hydrostannation of carbonyl bonds, which involves initial formation of a stannyloxy radical, followed by hydrogen transfer, is now demonstrated in the case of aldehydes [138]. Protonolysis of the Sn – O bond leads to the alcohol. In recent years the major effort has been devoted to the control of selectivity. A nice case of selective reduction of a multifunctional compound illustrates well the chemoselectivity of the process [139]. Other chemoselective processes have been found by reacting Bu_3SnH or Bu_2SnH_2 in the presence of several kinds of additives: phosphine oxides for the reduction of α -chloro-

carbonyl compounds to chlorhydrins [140], low-valent Ti [141] or SiO₂ [142] for the selective reduction of aldehydes, *p*-dinitrobenzene for the reduction in the presence of the C–Br bond [143], HMPA for reduction of haloketones at the carbonyl bond with trapping of the initial adducts to make heterocyclic compounds [144, 145]. Diastereoselective processes have been observed by addition of a number of catalysts: Lewis acids [146, 147], tetrabutylammonium salts [148], tributyltin triflate [149] and silica gel [150]. However, the catalysis with an optically active binaphthyl Lewis acid has only led to moderate enantioselectivity [151]. Some reversals of selectivity have been described. Thus, with α -alkoxyketones, Bu₃SnH–Bu₄NF is *syn*-selective while Bu₂SnHCl is *anti*-selective [152]. With α,β -epoxyketones, Bu₂SnHCl leads to aldols while Bu₂SnHF–HMPA gives *anti* reduction of the carbonyl [153].

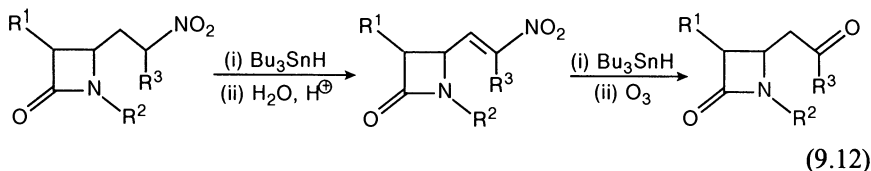
Finally, in a different area, a remarkable transformation of aldehyde into ketone has been described:



Similarly, PhCH(CH₃)CHO has been quantitatively transformed into PhCOCH₃ [154].

Reduction of carbon–carbon double bonds. In the case of simple alkenes, the usual behavior is hydrostannation, or *Z/E* isomerization [55, 154, 155], but there is one recent example of direct reduction (1-octene to octane) under yttrium catalysis [156]. Cases of C=C reduction in conjugated systems are more usual. Reductions of α,β -unsaturated carbonyl compounds, via 1,4-hydrostannation, have been reported for trifluoromethyl carbonyl derivatives [157] and in prostaglandine synthesis [158]. Et₃B is a good initiator for this process [159]. In a different procedure, hydridocuprates, generated *in situ* from Bu₃SnH and CuI–LiCl, give high reduction yields [160] and an indirect method involves tandem Michael addition of PhSH and Bu₃SnH reduction of the new C–S bond [161].

The 1,4-addition of tin hydrides to nitroalkenes constitutes a convenient route to nitroalkanes and, after oxidation, to carbonyl compounds as in the β -lactam series [162, 163].

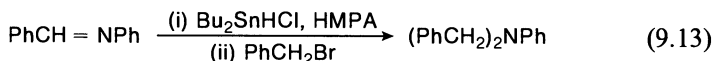


Finally, it is worth mentioning two unusual fragmentation processes, accompanying homolytic 1,4-hydrostannation of α,β -enones: one in the steroid series leading to aromatized 9,10-secosteroids [164], the other with removal

of an allylic or benzylic moiety by C–C bond breaking upon reaction of Wieland–Miescher ketones with Bu_3SnH [165].

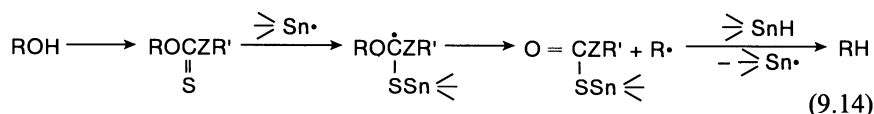
Reduction of other double bonds. Two cases of full desulfurization of $\text{C}=\text{S}$ to CH_2 have been reported [166, 167] the second being the transformation of thionoester, RCSOR' into ethers, $\text{RCH}_2\text{OR}'$, which constitutes an indirect reduction of esters, easily transformed into thionoesters. The reaction has been generalized with the use of Ph_3SnH instead of Bu_3SnH [168].

Examples of reduction of $\text{C}=\text{N}$ include the transformation of isothiocyanates RNCS into thioformamides, RNHCHS , with Bu_3SnH [169] and the reduction of imines to secondary amines with Bu_2SnHCl and HMPA [170]. In the latter case, the alkylation of the intermediate adduct, instead of protonolysis, allows a one-pot preparation of tertiary amines:



Nucleophilic or free radical addition of Bu_3SnH on azoarenes $\text{ArN}=\text{NAr}'$ can lead efficiently to hydrazoarenes, $\text{ArNHNHAr}'$ [171]. Also, 1-methylquinolinium ions undergo regioselective 1,2- or 1,4-reductions via a polar mechanism or photoinduced electron transfer [172].

Hydrostannations followed by fragmentation or elimination. The Barton reactions for the reduction of ROH to RH , via thiocarbonyl derivatives, are certainly amongst the more popular reactions. They function via addition of a stannyl radical to $\text{C}=\text{S}$ followed by fragmentation [173–175].



Et_3B -air catalysis is efficient [174, 176, 177] and the use of polystyrene-supported organotin hydride improves the work-up. Bis-deoxygenation can be performed through cyclic thionocarbonates [178, 179]. A comparison of various phenoxythiocarbonyl derivatives, ROCSOAr , with xanthates, ROCSSMe , has shown that the latter are especially reactive [180], although when Ar is C_6F_5 , very good efficiency is reached [181] particularly for the deoxygenation of primary alcohols [182]. Even tertiary xanthates can be isolated and reduced in high yields using various types of radical initiation [183, 184].

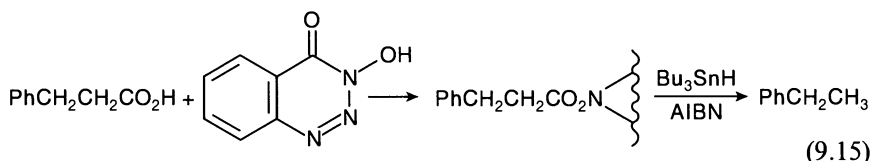
In a related type of reaction, deoxygenation of alcohols has been performed in high yields through thioxocarbamates [185], PhNHC(S)OR , themselves conveniently prepared by addition of alcohols to phenyl isothiocyanate or through *N*-acylthioxocarbamates, R'CONHC(S)OR [186].

Some unexpected results may occur in Barton's deoxygenations. Thus,

bond angle strain energy may promote selective homolytic cleavage of primary over secondary C–O bond in cyclic thionocarbonates [187]. In addition, some 1,3-bis(phenoxythiocarbonyl) derivatives, in the pyranoside series, have lead to partly reduced compounds, instead of the expected bis-deoxygenated products, because of the interaction of the radical formed in the first fragmentation with the second thiocarbonyl moiety [188]. On the other hand, the expected 1,2-elimination to olefin occurs when a phenylthio group is vicinal to the thiocarbonyl moiety [176].

Other synthetic transformations involving initial addition to C=S and fragmentation have been applied to the reduction of acyl chlorides, RCOCl , to aldehydes, RCHO , through intermediate 1-acyl-3-methylimidazole-2-thiones [189] and to the synthesis of nitriles, $\text{RR}'\text{CHCN}$, from ClCH_2CN via homolytic desulfurization of α -dithiocarbamoyl nitriles [190].

Initial addition of tin radicals to C=O bonds may also lead, after fragmentation, to valuable synthetic processes. Thus acyl derivatives of hydroxamic acids are a source of carbon radicals as in the following transformation [191]:



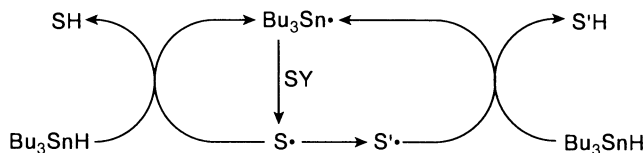
In addition tertiary propargyl alcohols have been deoxygenated after esterification with methoxalyl chloride ($\equiv\text{C}-\text{OH} \rightarrow \equiv\text{C}-\text{O}-\text{CO}-\text{CO}_2\text{Me} \rightarrow \equiv\text{C}^\cdot + \text{Bu}_3\text{SnO}_2\text{C}-\text{CO}_2\text{Me}$) [192] and trisubstituted alkenes have been stereoselectively obtained by the following sequence: allylic alcohol, xanthate, dithiocarbamate (through [3,3]sigmatropic rearrangement) and reduction [193].

Finally, azido compounds RN_3 can be transformed in high yields into amines, RNH_2 , via Sn–N intermediates, as shown in the preparation of amino and diaminodeoxynucleosides [194, 195].

9.1.4 Reductions with rearrangements

A large number of free radical rearrangements (translocations, ring openings, ring closures, tandem reactions, cascades) have been initiated and studied via organotin reagents. It is certainly true to say that organotin chemistry lies at the heart of the present extraordinary renewal of interest in radical processes in synthetic organic chemistry. An exhaustive review of several hundred papers, in the last few years, is not possible in a limited amount of space. Instead, we will focus on a reasonable number of selected recent results which demonstrate new advances, especially useful synthetic strategies and which use all the possible methods to gain entry into free radical chemistry through organotin hydrides.

The general scheme for reactions of a substrate SY with rearrangement, in the case of the popular reagent Bu_3SnH , involves the following steps:

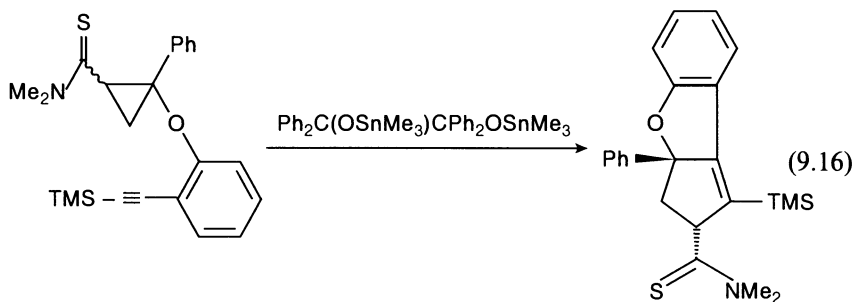


Scheme 9.1

In most cases it is necessary to perform extensive rearrangement of S' to S'' , for which low concentrations of Bu_3SnH are necessary, a situation usually reached with high dilution by very slow addition of Bu_3SnH via a syringe pump device or by generating $\text{Bu}_3\text{Sn}\cdot$ from sources different from Bu_3SnH , such as bis(tributyltin)benzopinacolate [37, 38]. However, it is not always easy to prevent the formation of more or less important quantities of SH. On the contrary, it may be synthetically useful to trap S' before it rearranges and for that purpose high concentrations of Bu_3SnH are necessary. A recently published method to prevent slow rearrangements employs catalytic amounts of diphenyldiselenide, which is reduced to PhSeH , an extremely rapid hydrogen transfer agent [196].

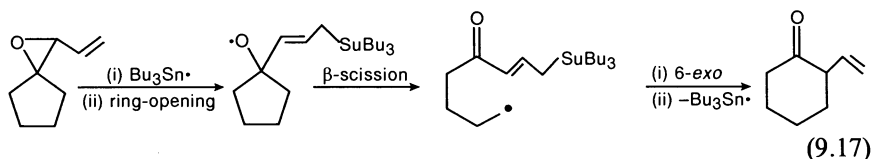
Ring opening reactions

Cyclopropylcarbinyl to 3-butenyl and cyclobutylcarbinyl to 4-pentenyl radical. Examples of ring opening of bicyclo[4.1.0] and [3.1.0] systems to cyclohexene and cyclopentene [197–199] have been published. An aza variant, by addition of $\text{Bu}_3\text{Sn}\cdot$ on the carbonyl oxygen of *N*-acylaziridines, leading to amides, is also documented [200]. The intermolecular trapping of the rearranged 3-butenyl radical with an alkene, followed by 5-*exo* cyclization gives an entrance to five-membered rings [201, 202]. More complex rearrangements involve ring opening and intramolecular addition to give spirocyclic quaternary centers [203] and cascades of rearrangement such as [204]:



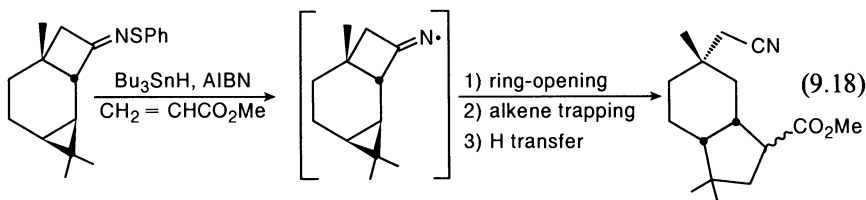
A bicyclo[4.2.0] system has been transformed into a cyclooctane ring by a two-carbon expansion [205] and a complex tandem ring opening/ring expansion has also been observed [206].

Oxiranylcabinyl to allyloxy and oxetanylcabinyl to 3-butenyloxy radical. This ring opening occurs in the reduction of α,β -epoxyketones to alcohols (via initial addition of $\text{Bu}_3\text{Sn}^\bullet$ at the carbonyl oxygen [207]), but in many cases the opening follows also a different route by C–C cleavage when, for instance, a phenyl group can stabilize the incipient vinyloxy-substituted carbon-centered radical [208, 209]. This unusual orientation of ring opening, in the case of ring-fused substrates, leads to medium-sized oxygen heterocycles [210, 211]. More complex processes in which the ring opening is followed by fragmentation (β -scission of alkoxy radicals) and sometimes other rearrangements lead to medium-sized rings [212] or cyclohexanones [213].



Some cases involve also further steps such as 1,5-H transfer and 1,5- SnBu_3 transfer [118, 214, 215]. The addition of $\text{Bu}_3\text{Sn}^\bullet$ to a vinyl oxetane is accompanied by ring opening and 1,6- SnBu_3 transfer, leading to an allylic radical [216].

Miscellaneous. The aziridinylcarbiny to allylaminy radical rearrangement, which may be accompanied by cleavage in the other sense [217, 218] has a synthetic interest to obtain pyrrolidines when a double bond is suitably placed for a further 5-*exo* ring-closure [219]. Also, a general approach to condensed thiophenes takes place via an internal ring opening of a ketene dithioacetal by an aromatic radical followed by a further step of addition–elimination [220]. Finally, cyclobutyl and cyclopentyl iminyl radicals, generated from *S*-phenyl sulfenylimines, undergo ring openings which can enter into impressive cascade reactions such as the following [221]:



Cyclization reactions

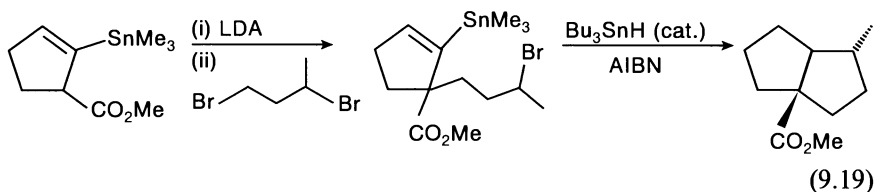
Addition of carbon-centered radical to C=C.

3-Butenyl to cyclopropylcarbinyl radical. A ring expansion from cyclopentane to cyclohexane derivatives has been observed, although in moderate yield, by ring closure/ring opening, upon thermodynamic control, of a 3-butenyl radical [222].

4-Pentenyl to cyclobutylcarbinyl or cyclohexyl radical. With suitable substituents, the 4-*exo* cyclization can occur at a synthetically useful rate [223, 224]. β -Lactam ring closure from *N*-ethenyl α -bromoalkanamides illustrates this finding [225, 226]. The 5-*endo* process, although usually disfavored, has been successfully applied to the synthesis of five-membered lactams from 2-chloro-*N*-(cyclohexen-1-yl)acetamides [227].

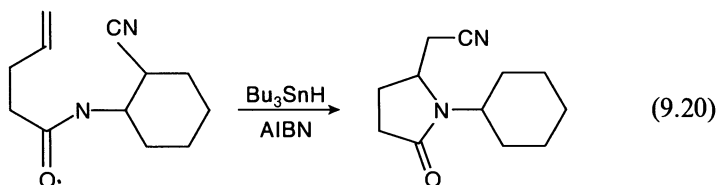
5-Hexenyl to cyclopentylmethyl or cyclohexyl radical. The 5-*exo* ring closure is certainly the most common process. Numerous examples are described with more or less substituted radicals, generated by different methods, undergoing intramolecular additions on a variety of substituted alkenes. A representative case of radical generated by carbon-halogen bond substitution, leading to stereocontrolled functionalized fused carbocycles has been published recently by Curran [228]. Also, cases of cyclization to *C*-furanoside [229] or to lactams related to natural products [230] are worth mentioning.

A special citation should be made to two general and fruitful approaches. One is the temporary silicon connection method popularized by Stork, in which cyclization of allyloxydimethylsilylmethyl radicals is followed by the oxidation of Si-C bonds to give polyols [231, 232]. The other is the internal addition of a carbon-centered radical to a vinyl-tin bond, which ends up with the removal of a stannyl radical, achieving a catalytic process [233, 234]:

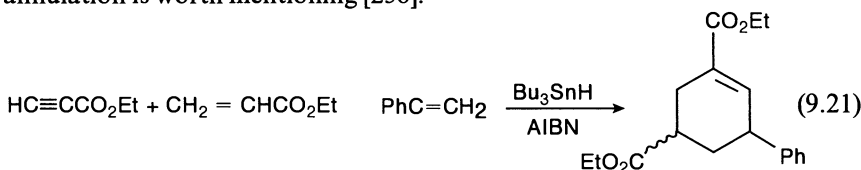


Examples of radicals promoted by C-S bond cleavage are numerous. They include the use of ω -ethylenic oxothiolanones for the synthesis of cycloalkanols [235], carbon-centered radicals derived from glycine for the synthesis of cyclic α -amino-acids [236] and the ring closure of precursors of carbapenem antibiotics [237]. Cyclizations following C-Se bond cleavage can be exemplified by the synthesis of stereocontrolled substituted tetrahydrofurans [238] or functionalized bicyclic carbocycles [239]. *O*-stannyl ketyls, obtained by addition of Bu_3Sn^+ to aldehydes or ketones, can also undergo cyclization to cycloalkanols [240] or chiral pyrrolidines [241], or lead to

hydrodimerization of α,β -enones [242]. Also, the intermediate adducts of $\text{Bu}_3\text{Sn}^\cdot$ on $\text{C}=\text{S}$ bonds, in the Barton–McCombie reactions, can be intramolecularly trapped, either before fragmentation, to give cyclic thionocarboxylic acid derivatives [243, 244], or after fragmentation [245, 246]. Suitably built precursors allow interesting cascade reactions leading to polycyclic compounds [247]. They enable the generation at high yield of complex architectures such as cedrene [248] and triquinanes [249, 250]. Very impressive transformations can occur [251], such as the following sequence in which there is successively 5-*exo* cyclization to $\text{C}=\text{C}$, 5-*exo* cyclization to $\text{C}=\text{N}$ and $\text{C}-\text{C}$ bond cleavage of iminyl radical [252]:



The 6-*endo*-trig process, although less usual than the previous one, is active in several synthetic processes, especially when it produces a stabilized radical [253]. The carbacephem six-membered ring has been built accordingly [254]. Chloroethylsilyl enol ethers [255] and bromomethylsilyl ethers of allylic alcohols [256] give the same type of ring closure, while tandem reactions to polycyclic systems are also observed [257]. A nice case of three-component annulation is worth mentioning [258]:



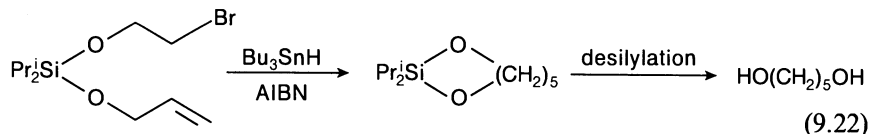
Its success lies in the initial addition of $\text{Bu}_3\text{Sn}^\cdot$ at the triple bond, followed by addition of the incipient radical to the more electrophilic alkene; the newly formed electrophilic radical adds to the nucleophilic alkene and the process is completed by β -elimination of $\text{Bu}_3\text{Sn}^\cdot$ after a 6-*endo* cyclization.

6-Heptenyl to cyclohexyl radical. Representative examples are the cyclization of 7-deoxy-7-iodohept-1-enitols to analogs of sugars [259], the synthesis of branched chains cyclitols [260] and cases of transannular cyclizations [261]. An allenic system can be the end-point of cyclization [262].

The 6-*exo* ring closure of *O*-stannyl ketyl radicals (addition of $\text{Bu}_3\text{Sn}^\cdot$ to carbonyls) can occur either in the case of electron-rich [263] or -poor [264] olefins. Finally, a regiospecific radical annulation strategy to functionalized chiral bicyclo[3.3.1]nonanes involves a $\text{Bu}_3\text{Sn}^\cdot$ promoted intermolecular Michael addition followed by a 6-*exo* intramolecular Michael addition [265].

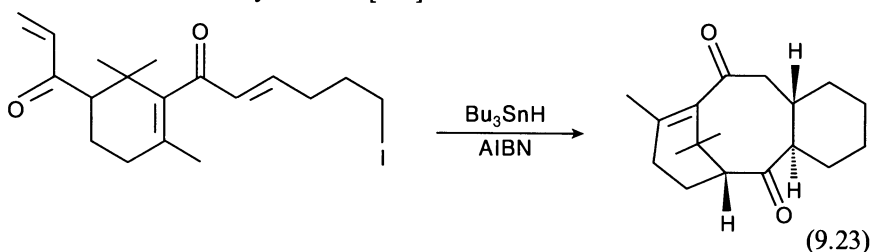
Macrocyclizations. Long range cyclization of carbon centers on radicophilic

sites is a specially interesting process. For instance, *endo* cyclization to seven, eight or nine-membered ring protected diols occurs with substrates containing a silaketal ether [266], as in the following example:



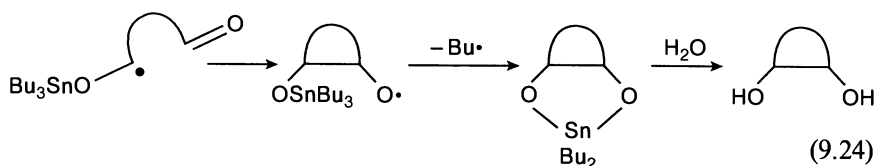
Eight to 16-membered macrocyclic lactones [267], 14-membered cembranoids [268], macrocyclic ketones [269] or nitriles [270] have all been efficiently obtained in one step from acyclic precursors. A beautiful high-yield synthesis of a series of macrocyclic α -methylene lactones involves acyclic seleno allyltins, $\text{CH}_2=\text{C}(\text{CH}_2\text{SnBu}_3)\text{CO}_2(\text{CH}_2)_n\text{SePh}$ ($n=6-11$), in which Bu_3SnH -AIBN provides the C-Se cleavage, followed by intramolecular addition to $\text{C}=\text{C}$ and β -elimination of Bu_3Sn^+ [271].

Also, spectacular results have been obtained in tandem reactions in which the initial macrocyclization is followed by one or several transannular radical processes leading to ring-fused bicycles [272] and tricycles [273], including an access to the taxane architecture by a tandem 12-*endo* macrocyclization and 8-*endo* transannular cyclization [274]:

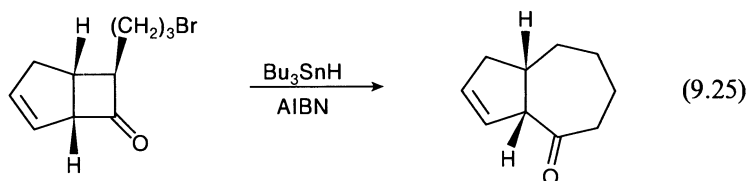


Miscellaneous. *N*- ω -Iodoalkyl indoles, with a good leaving group in the 2-position, are reduced to give a variety of fused [1,2-*a*] indoles [275].

Addition of carbon-centered radical to C=O, C=N or C=S. In some cases it is possible to trap the O-centered radical arising from the *n-exo* cyclization to $\text{C}=\text{O}$ before it reopens. Thus cyclohexanols [276, 277] and cyclopentanol derivatives [278] have been prepared in good yields. An interesting recent case describes the intramolecular pinacol coupling of dialdehydes and ketoaldehydes, giving *cis*-diols by a process in which the addition of Bu_3Sn^+ on a carbonyl bond is followed by the formation of a dibutylstannylene derivative via abstraction of one butyl group on tin [279].

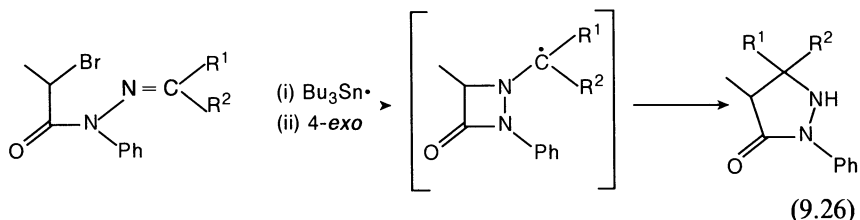


However, in most situations the cyclization is followed by reopening of the ring, which can be reoriented by adequate substituents [280], for instance to give a formal ring expansion, a process intensively studied by Dowd. For instance, 1-carbon ring expansion occurs through an intermediate C-3 oxyl radical [281], a transformation efficiently performed with a polystyrene-supported organotin hydride [282]. More complex versions include tandem reactions to give polycyclic systems [283]. Longer free radicals allow more extensive ring expansion, for instance $C_4 \rightarrow C_7$ [284] or $C_{12} \rightarrow C_{15}$ as in a synthesis of muscone [285]:



In a similar way, various sizes of ring expansion, with the concomitant introduction of a C=C bond in the cycle, are efficiently obtained using Baldwin's general process in which a suitably placed Bu_3Sn group is removed in the reopening step, providing a reaction catalytic in tin radicals [286].

In the case of C=N terminus, the 3-*exo* cyclization gives an α -cyclopropylaminyl radical which reopens in the sense of the higher thermodynamic stability [287]. More synthetic interest exists with 5-*exo* processes leading to cyclopentane rings [288]. The same is true when the terminus is a hydrazone [289] or an oxime ether [290]. The internal addition of a C radical to *N*-aziridinyl imines is followed by an interesting fragmentation step [291, 292] while a cyclization to the *N* atom of a C=N bond occurs in the reaction of α -bromoacylated phenylhydrazones and leads to 2-phenylpyrazolidin-3-ones in excellent yields [293]:



In a related way, iodoalkylpyridinium salts undergo cyclization to tetrahydroquinolizinium salts via an intermediate dihydropyridine which is rearomatized by air oxidation [294].

Finally, an addition to C=S has been observed in an attempted double Barton reduction of a bis-xanthate in which the initially formed carbon radical cyclized on the C=S bond of the second xanthate group to give a dithioketal [295].

Addition of carbon-centered radical to $C\equiv C$ and $C\equiv N$. There are numerous cases of successful 5-hexynyl to methylene cyclopentane radical rearrangements and their heterocyclic analogs (5-*exo*-dig) [296]. It is worth mentioning the use of the temporary connection of a phenylethynyl group to a carbohydrate, through a silicon atom, for the stereospecific synthesis of C-glycosides [297] or the similar attachment of a bromodimethylsilyl group to propargylic alcohols before cyclization [298].

6-*Exo*-dig ring closures have been also successful [297, 299] while *endo*-dig processes are efficient in the case of macrocyclization of ω -iodoalkyl propiolates [300]. 6-*Exo*-dig ring closures on $C\equiv N$ have been employed for the synthesis of carbazoline derivatives [301].

Addition of vinyl carbon radical to $C=C$, $C=X$ and $C\equiv C$. A number of vinyl radicals, generated by the terminal addition of Bu_3Sn^\cdot on $C\equiv CH$, have led to five-membered ring systems by intramolecular addition to $C=C$ (5-*exo*). In general the cyclized vinyltin undergoes easy protonolysis to the corresponding *exo*-methylene derivative. Representative and recent examples are found for the synthesis of intermediates in the synthesis of avermectins [302], optically pure sulfoxides [303] and in carbohydrate synthesis [304]. The vinyl radical can be also generated by halogen abstraction from a vinyl bromide [305].

Six-membered rings are also synthesized by 6-*exo* processes, as in a highly diastereoselective cyclization using chiral α,β -unsaturated esters as end-point [306] or the high-yield synthesis of *trans*-hydrindanes [307]. An unusual bromoenyne radical cyclization to cyclopentenyne products can also be cited [308], as well as an example of tandem cyclization [309] and a surprising intramolecular addition to furans, followed by ring opening of a spiro radical which offers a new route to cyclopentene rings, models of prostaglandins [310]. The $C=N$ bond of oximes ethers is able to add internally vinyl radicals generated by hydrostannylation of alkynes [311] or allenes [312]. In both cases, the vinyl-tin bond is subsequently protonolyzed. Similarly, vinyl radicals, obtained from vinyl bromides, allow the construction of bi- and tricyclic systems of different sizes [313].

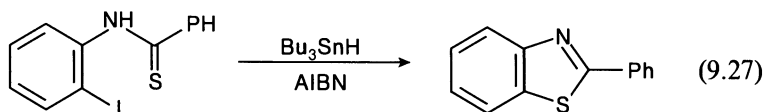
The same type of reaction is observed with $C=O$ bonds, but in some cases the intermediate alkoxy radical undergoes fragmentation and recyclization, as in a new method for synthesizing fused cycloheptanones and cyclooctanones from substituted cyclohexanones [314].

As expected, it is possible to obtain five-membered rings by a 5-*exo* process to $C\equiv C$ [315], and this type of cyclization can be adapted to tandem reactions giving new allyltins after a further hydrostannylation step [316].

Addition of other unsaturated radicals to $C=C$. A number of acyl radicals, generated from phenylselenoesters, have been cyclized to give cyclanones of different sizes, incorporating heteroatoms if desired. Crich has been particularly active in this field [317, 318]. The reactions are especially stereoselective for the synthesis of *cis*-2,5-disubstituted tetrahydrofuran-3-ones [319] and

they can be applied to macrocyclization [320], and tandem processes [321]. Similar cyclizations from selenocarbonates lead to γ - or δ -lactones [322]. Imidoyl radicals are cyclized to various heterocycles [323], a nice example being a novel indole synthesis from olefinic isonitriles [324]. Iminyl radicals, generated from sulfenylimines [325] or oxime esters [326], give pyrrolenines in high yield by 5-*exo*-trig cyclizations on C=C bonds.

Addition of aromatic carbon radical to X=Y. There are numerous cases of cyclization of an aromatic radical, generated by halogen abstraction, on a suitably placed C=C bond to give five, six or seven-membered carbocycles [327–329] or heterocycles [330–332]. Ring closures on C=O [333], C=N [334] and N=N [335, 336] are also known. Special situations include a cyclization on the C=S bond of thioamides which is accompanied by oxidation, possibly via a pseudo- $S_{RN}1$ mechanism [337]:

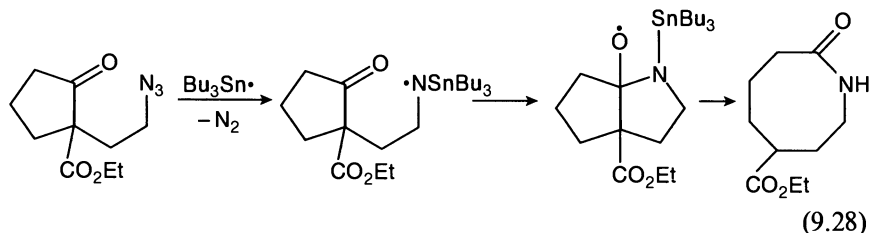


Tandem cyclizations can occur, as in the synthesis of lysergic acid derivatives [338] or benzoprostacyclins [339]. The cyclizations can be followed by intermolecular addition [340] or other rearrangements [341]. Heteroaromatic substrates, such as imidazoles, also may undergo cyclizations [342].

Addition of aromatic carbon radical to aromatic ring. Some cases of efficient aryl-aryl couplings induced by Bu_3SnH are known [343–345], leading to fused polycyclic systems, although the mechanisms are not always clear. Similar coupling can occur at a heteroaromatic terminus such as a pyrrole ring [346].

Addition of heteroatom-centered radical to X=Y. Amidyl radicals, produced by homolytic cleavage of N–O in *N*-hydroxypyridine-2-thiones imidate esters with Bu_3SnH , undergo 5-*exo* cyclization [347] while aminyl radicals, generated from diunsaturated sulfenamides precursors, give pyrrolizidines by a 5-*exo* followed by a second 5-*exo* or 6-*endo* closure [348]. More complex cascades have been reported from amidyl radicals generated from *O*-benzoyl hydroxamic acid derivatives [349].

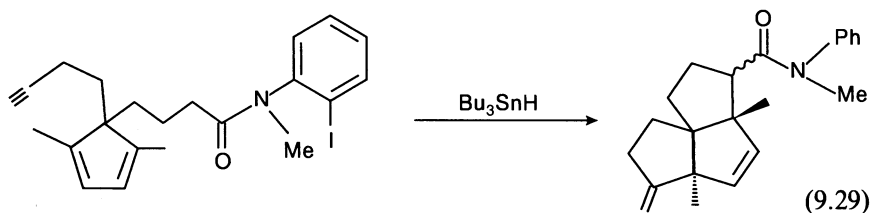
Aminyl radicals are able to add to a carbonyl group, a reaction followed by ring opening which finally produces ring-expanded lactams [350]:



A very curious acceleration by $\text{Bu}_3\text{Sn}_2\text{O}$ of the 5-*exo* cyclization of aminyl radicals to C=C has been reported [351].

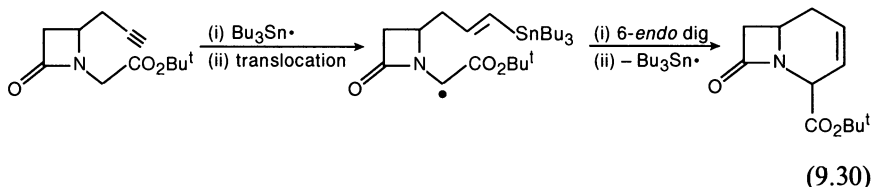
Translocations

There are a number of examples of 1,2-acetoxy group shift, in carbohydrate chemistry, after initial radical dehalogenation at the anomeric position [352]. Also, a 1,2-nitrate shift occurs in the Bu_3SnH reduction of $\text{BrCH}_2\text{CH}(\text{Ph})\text{ONO}_2$, which gives $\text{PhCH}_2\text{CH}_2\text{ONO}_2$ [353], and the reduction of α -aryl- β -bromoalkylvinylethers to δ -acyl ketones involves a new C-C bond-forming rearrangement [354]. Xanthate reductions with 1,2-hydrogen shifts and transannular translocations are also known [355] as well as 1,5-hydrogen shift on alkoxyl radicals generated by Bu_3SnH reduction of nitrate esters [356]. Various 1,5-H transfer from *ortho*-halogeno benzamides, followed by intramolecular cyclization or intermolecular trapping with activated C=C are known [357–359]. The conversion of α - to β -mannopyranoside results from a 1,5-H transfer involving the anomeric position [360]. Also, *ortho*-halogeno anilides undergo different types of 1,*n*-H transfers [361, 362], a particularly spectacular example being the access to the polyquinane family via cascade cyclization after initial translocation from an aryl radical to an α -amidoyl radical [363]:



Curran has developed self-oxidizing protecting groups, for instance for the oxidation of $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH}$ to $\text{PhCH}_2\text{CH}_2\text{CHO}$, which work via a 1,5-H transfer from an initially formed aryl radical [364].

1,5-H transfer to vinylic radicals has been used in a new route to spiroketals [365] or bicyclic β -lactams [366]:



Radical isomerization via intramolecular *ipso* substitution of *N*-aryl amides (aryl translocation from N to C) [367] and aryl ethers (aryl translocation from O to C) [368] have found synthetic uses, after halogen abstraction

by Bu_3Sn radical. It is worth mentioning also the *ipso* substitution of homopropargyl arenesulfonates which, after addition of $\text{Bu}_3\text{Sn}^\cdot$ on $\text{C}\equiv\text{C}$, finally leads to sulfones [369].

9.2 Applications of tin-carbon bonded compounds

9.2.1 Transmetallation reactions

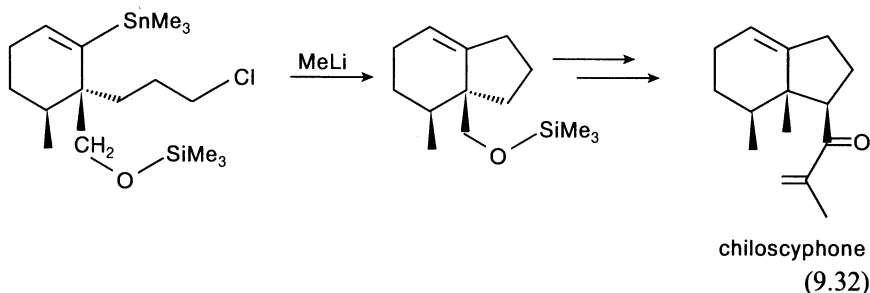
Transmetallations with lithium reagents. Since their discovery by Seyferth [370] in 1957, transmetallations have proven to be very useful applications of unsymmetrically substituted tetraorganotins in organic synthesis for the preparation of organolithiums, organocoppers and organoborons. With lithium, it is a general reaction where a new organolithium is produced upon treatment of an organotributyltin or organotrimethyltin with butyl- or methyllithium, respectively. The reaction is of preparative use when the equilibrium of the reaction is driven completely to the right, i.e. when the stability of the formed organolithium is larger than that of butyl- or methyllithium, which is the case for vinyl, aryl, benzyl, allyl or heteroatom-substituted lithium reagents.



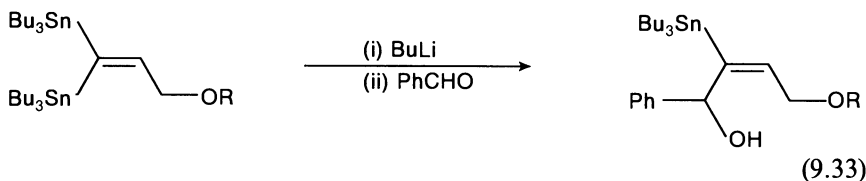
Transmetallation proceeds with retention of configuration at the carbon atom and its stereochemistry is solvent dependent on the tin. Retention is observed in ether, while epimerization occurs in THF [371]. It is usually a very fast reaction, even at low temperature, where carbonyls do not need protection. Transmetallation is faster than addition to ketones or epoxides. ω -Keto- [372] or ω -epoxy-2-alkenyltins [373] were cyclized by intramolecular addition of the corresponding lithium reagents prepared by transmetallation with butyllithium.

Vinylorganotins. Tin-lithium exchange of 2-trimethylstannylbutadiene [374] or (*Z*)- or (*E*)-1-stannylbutenyne [375] gives the corresponding 2-butenyl-lithium, or (*Z*)- or (*E*)-1-buten-3-ynyllithium, respectively, used in the synthesis of bicyclo[5.3.1]undecadienes necessary for the preparation of polyenyne. Treatment of 2,3-bis(trimethylstannyl)-1,3-butadiene with one equivalent of butyllithium, followed by one equivalent of electrophile gives 2-substituted-3-stannylbutadienes which can be lithiated a second time. 2,3-Distannyl-1,3-butadienes are thus 2,3-dilithio-1,3-butadiene equivalents [376]. ω -Halo-2-stannyl-1-butene, -pentene and -hexene are transmetallated to the corresponding lithium reagents without interference by the halide at low temperature. These bifunctional reagents enable the development of new methylenecyclopentane [377, 378], (*Z*)-ethylidenecyclopentane [379], methylenecyclopentane [380] and methylenecycloheptane [381] annulation methods

which were applied to the synthesis of sesquiterpenoids pentalene [378] and chiloscypnone [381].



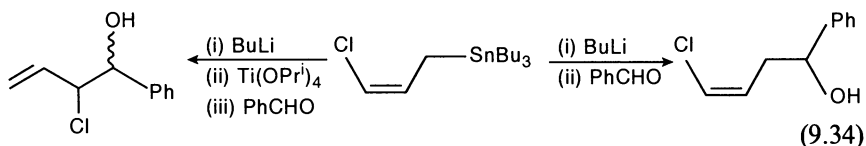
When transmetallated in the corresponding lithium reagents, vinyltins are useful intermediates in the synthesis of prostaglandins. They allow an easy introduction of the ω -side chain by 1,4-addition to a cyclopentenone unit [382–384]. An alternative method is coupling such a vinyltin-derived reagent with an iodomethylated Corey's lactone [385]. These later examples involve transmetallation of vinyltins, substituted by one or several protected hydroxyls. However, protection is not compulsory, as unprotected hydroxyls [386–388] or amines [389] do not interfere with the transmetallation process. A tin atom on a boron-substituted carbon can also be transmetallated. After reaction with aldehydes and elimination of boron hydroxide it leads to allenes [390]. Both tins in 1,1- or 1,2-distannylalkenes [391] can be successively transmetallated. They are thus equivalents of 1,1- or 1,2-dilithioalkenes, respectively. In 1,1-distannyl-3-(methoxymethoxyl)-1-alkenes or 1,1-distannyl-3-hydroxy-1-alkenes, the tin *syn* to the allylic oxygen is transmetallated first, the resulting lithium reagent being stabilized by lithium–oxygen complexation [392].



Steric effects are important features in transmetallation reactions. When a double bond in a chain is disubstituted by tin atoms at either side of the double bond [393], the more accessible external tin atom is transmetallated first, preferentially to the internal one. Another illustration of this sensitivity to steric hindrance is the unreactivity of vinyltins with a tetrasubstituted double bond towards transmetallation. However, this difficulty can be overcome by an iodination halogen-metal exchange process which gives tetrasubstituted vinyl lithium reagents in good yield [394, 395]. Transmetallation of

allenyltins, leading to an equilibrated mixture of allenyl- and propargyl-lithium allows a regioselective propargylation of aldehydes and ketones [396].

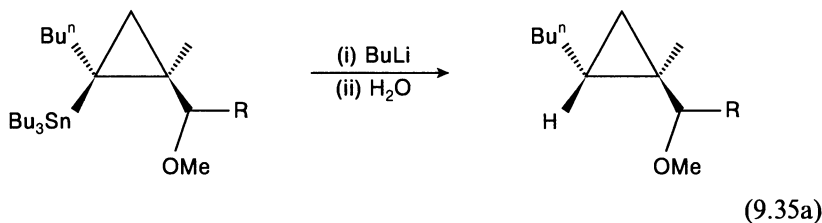
*Alkyl-, benzyl-, allyl-, aryl- and cyclopropylorganotin*s. Alkyl-, benzyl- [397], allyl- and aryltins are also precious sources of lithium reagents. One-pot monotransmetallation of distannylmethane, reaction with esters and then further transmetallation allows the transformation of esters in the corresponding methyl ketone [398, 399]. With ketones, methylenation is achieved [400]. One interesting example is (*Z*)-3-stannyl-1-chloro-1-propene which gives (*Z*)-1-phenyl-4-chloro-3-buten-1-ol upon treatment with butyllithium and benzaldehyde. Addition of titanium tetraisopropoxide prior to addition of benzaldehyde reverses completely the regioselectivity of the reaction to give 1-phenyl-2-chloro-3-buten-1-ol [401].

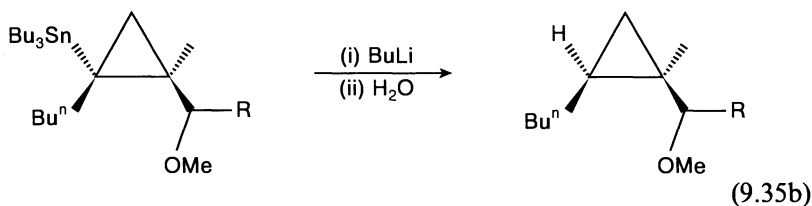


Double transmetallation of 4,7-distannyldihydropentalene leads to dilithium acepentalenediide [402].

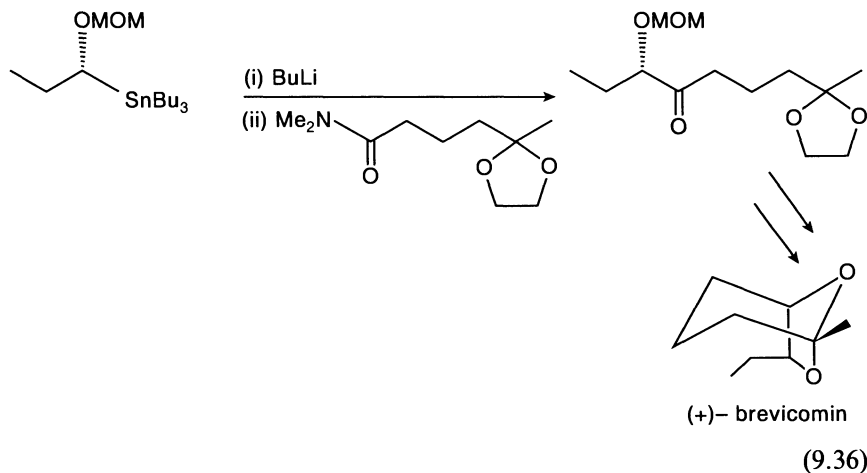
2,6-Dialkylated aromatic sulfones are obtained from treatment of the corresponding 2,6-distannylarylsulfone with two equivalents of butyllithium and alkylating agent [403]. Chromium tricarbonyl aromatic complexes do not interfere in the transmetallation of chromium-complexed substituted aromatic tins [404]. Two successive metallation-alkylation processes allow easy access to 3,4-unsymmetrically substituted furans from 3,4-bisstannyl-furans [405] and to 1,4-disubstituted benzenes from 1,4-bisstannylbenzene [406].

Selectivity in the transmetallation of cyclopropyltins is not affected by the complexation of the resulting lithium reagent by a chelating group. Thus, both isomers of 2-stannyl-2-(phenylthio)cyclopropanecarboxamides [407] and methoxy-1-(2-stannyl-2-alkyl-cycloprop-1-yl)ethane [408] are transmetallated without epimerization, even if one of the prepared lithium reagents is more stable than the other. The rate of the reaction is higher for the *syn* isomer.



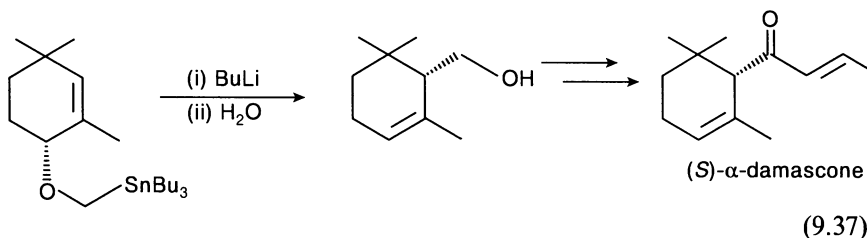


(*Alkoxy- and haloorgano*)organotins. Alkoxy substitution at an aliphatic carbon-bearing tin weakens the carbon–tin bond and allows easy nucleophilic attack of lithium reagents. It is a general reaction, regardless of substitution at the carbon, providing that 1,2-dimethoxyethane is used instead of THF [409]. Further reaction with copper salts gives α -alkoxyalkylcoppers in high yield [410]. Intramolecular reactions of the lithium reagent thus formed with amides or allylic ethers are used in the stereospecific construction of bicyclic 3-(2*H*)furanones [411] or bicyclo[5.3.0]decenes [412], which emphasizes the chemoselectivity of transmetalation. It has been known for some time that optically active α -alkoxyallyltins, readily available by asymmetric reduction of acyltins, are stereoselectively transmetalated to the corresponding chiral lithium reagents. This interesting feature was successfully implemented in the synthesis of (+)-*endo*- and (–)-*exo*-brevicomins [413],



(*S*)-hexanolide [414], pleichrone and calphostine A [415], α -hydroxyacids [416, 417] and diols [418] with very high enantiomeric excess. Transmetalation of α -alkoxytins is also diastereoselective, as shown in the transmetalation of *cis*- and *trans*-3-alkoxy-2-tributylstannyltetrahydrofurans which gives the corresponding pure diastereoisomers [419]. This reaction is used with equal success in glycoside chemistry [420], where 2-hydroxyl [421] or 2-acetamido [422] protection is not required. α -Silyloxymethyltins do not give the corresponding lithium reagents upon reaction with lithium reagents. An intramolecular

reverse [1,2]-Brook rearrangement occurs, leading to an α -hydroxymethylsilane. With optically active α -siloxyethyltins, the rearrangement exhibits complete retention of configuration and is a useful entry to optically active α -hydroxysilanes [423]. The [1,4] version of the same rearrangement shows the same properties [424]. α -Alkoxyethyltins are common starting materials for the study of $[n,m]$ -Wittig–Still rearrangements, which are applied in the synthesis of (*S*)- α -damascone [425]



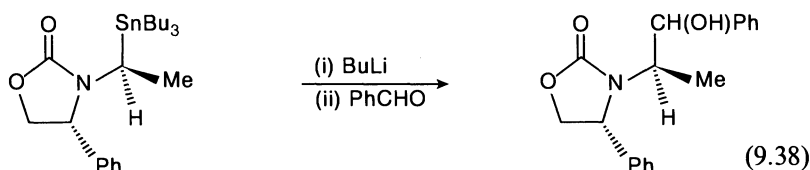
and alkene dipeptide isosteres [426]. Mechanistic studies conducted with optically active starting materials show that the rearrangement is a very highly stereoselective reaction allowing the synthesis of chiral allenes [427]. It occurs with inversion at the lithium center [428, 429] (the opposite of the reverse [1,2]-Brook rearrangement) and retention at the migrating center. When substituted α -epoxytins react with one equivalent of butyllithium [430] they are stereospecifically transmetallated without ring opening. With 2 equivalents of base, reductive alkylation gives a disubstituted alkene [431]. Unsaturation at the carbon bearing the metal is compatible with metal–metal exchange as transmetallation of α -alkoxyalkenyltins is easily [432] and stereospecifically [433] accomplished upon treatment with lithium reagents. It has been applied in a synthesis of jaspamide [434]. The presence of two heteroatoms on the same carbon is also compatible with this useful reaction, where better results are obtained when both the heteroatoms are in a ring [435]. Optically pure 2-stannyloxazolidines behave, after transmetallation and alkylation with aldehydes, as a chiral formyl anion equivalent [436, 437].

The presence of an oxygen in a γ -position from the tin also weakens the tin–carbon bond and allows an easy transmetallation with lithium reagents. Useful chiral lithium reagents are obtained from optically active γ -(secondary alkoxy)tins [438], while with a γ -mesylate a stereospecific internal displacement occurs leading to cyclopropanes [439].

The configurational stability of 1-bromoalkyllithiums prepared via transmetallation of the corresponding (1-bromoalkyl)tins is shown through stereochemical studies. It is assumed that tin–lithium exchange occurs with retention at carbon [440].

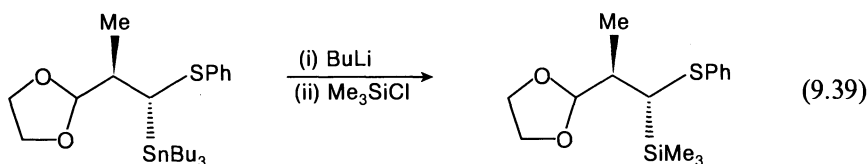
Nitrogen-containing organotins. Nitrogen-substituted carbanions are also available through tin–lithium exchange from nitrogen substituted organotins. Various allylic tertiary amines are obtained from the transmetallation

of γ -aminovinyltins which provides a convenient three-carbon homologation method [441]. Nitrogen can be brought closer to the carbanionic center with equal success in transmetallation. With an easily removable protecting group, transmetallation and reaction with electrophiles give substituted primary amines [442]. Substitution at the carbanionic center gives chiral organotinins which, when nitrogen is part of an imidazolidin-2-one or oxazolidine-2-one ring, or with 2-stannylpyrrolidine [443], are transmetalated with total retention of configuration [444].



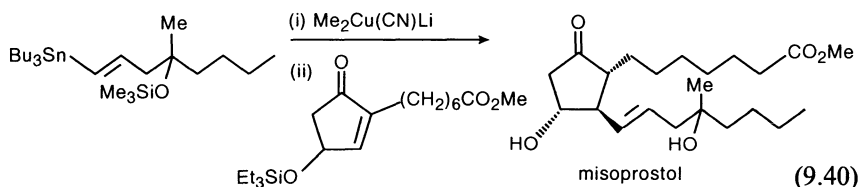
Acyclic substitution at nitrogen leads to equally good results [445]. However, configurational stability of such carbanions is lower than that of their oxygenated analogs [446], very low temperature and short reaction times being necessary to obtain high enantiomeric excess. The stannyl- β -lactams with unprotected nitrogen can also be transmetalated, providing that 2 equivalents of butyllithium are used [447]. When transmetalation of (2-azaallyl)stannanes is conducted at low temperature to avoid oligomerization of the corresponding 2-azaallyllithium [448], a smooth [4 + 2] cycloaddition with various alkenes or alkynes leads to substituted pyrrolidines [448, 449], 1-pyrrolines and pyrroles [450]. Imidoystannanes are transmetalated by lithium reagents at low temperature without reaction at the carbon–nitrogen double bond to give substituted imines after quenching by electrophiles [451, 452]. Hydrolysis of the imine group gives ketones, which makes imidoystannanes useful acyl anions equivalents. Transmetalation of 3-stannylated enamines followed by allylation and hydrolysis gives 3-substituted ketones which can be an alternative to 1,3-allylation of α,β -unsaturated ketones by cuprates [453].

Sulfur-containing organotinins. As with oxygen or nitrogen, the presence of a sulfur atom in a group linked to tin weakens the corresponding tin–carbon bond, which can then be subject to cleavage by lithium reagents. Despite the low configurational stability of the resulting α -(aryltio)alkyllithium reagents [454], transmetalation occurs with retention at carbon in α -(aryltio)alkyltins [455].



Two successive metallation-alkylation sequences have proved that a 1,1-distannylated dithiane is a useful methanol dianion equivalent used in the synthesis of roflamycin [456]. Transmetallation of bis(stannylmethyl)sulfide provides bis(lithiomethyl)sulfide, a new stable 1,3-dilithiated building block [457]. α -(Phenylthio)alkenyltins are easily transmetallated with retention of configuration to give the corresponding lithium reagents which can either be used directly [458] or transformed in organozinc with zinc dibromide [459]. The transmetallation proceeds equally well with 2-stannylated dihydrothiophene [460].

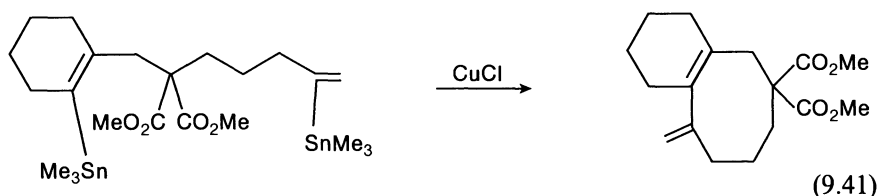
Transmetallation with copper reagents. Direct transmetallation with copper, either stoichiometric or catalytic, is one of the more interesting features of transmetallation studies of the last few years. Sometimes, the lithium reagents necessary to prepare organocuprates do not tolerate the presence of carbonyls of aldehydes and ketones, thus implying tedious and yield-lowering protection-deprotection steps. That is why any functionality-respecting reactions are welcome. It was first shown that allyl- [461], vinyl- [462, 463] and α -alkoxyalkenyltins [464] are transmetallated by high order organocuprates, avoiding the use of alkylolithiums. The usefulness of this method is exemplified in the synthesis of the misoprostol prostaglandin [462].



Then, intramolecular coupling of vinyltins and vinyl halides was shown to be conveniently accomplished in the presence of 2.5 equivalents of copper chloride. Iodides or bromides can be used in this process, which is suitable to build four-, five- or six-membered rings, and tolerates the presence of functional groups like alkoxycarbonyl or hydroxyl [465]. The possible involvement of vinylcopper reagents in this reaction is reinforced by the report of intramolecular conjugate addition of vinyltins to α,β -unsaturated enones, controlled by stoichiometric amounts of copper chloride [466], and by the observation that, in very polar solvents, copper iodide reacts with vinyltins [467]. Homocoupling of various vinyl-, aryl- or alkylvinyltins in the presence of stoichiometric amounts of copper(II) nitrate [468] is possible even in the presence of a free hydroxyl group and is a competitive method for the preparation of macrocyclic dilactones [469].

Intermolecular coupling between vinyltins and allylic halides proceeds in the presence of copper iodide under catalytic conditions. Substituted allylic halides lead to the coupling product with the more substituted double bond with a very high selectivity [470]. Free hydroxyl or carbonyl groups do not

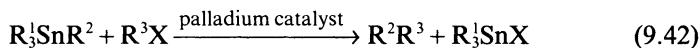
interfere with the coupling. Catalytic amounts of copper salts are also able to mediate the cross-coupling of α -heteroatom-substituted organotins with allylic or aromatic halides. Neighboring thio substituents, either on the organometal or on the halide, enhance yields and reaction rates. The reaction occurs with retention of configuration at the α -stannyl carbon [471], which is the expected behavior for a tin-metal transmetallation, as with lithium reagents, and contrasts strongly with palladium-catalyzed Stille reactions where complete inversion is observed [472]. When no halide is present, treatment of vinyltins with copper chloride gives 1,2-butadienes [473]. 2, n -Distannyl-1, n -dienes cyclize to give four to eight-membered cycles depending on the value of n [474].



Transmetalation with boron reagents. Vinylboranes are often volatile pyrophoric substances which are quite unpleasant to handle. This can be avoided by the use of transmetalation between bromoborane and vinyltin, which leads to solutions of vinylborane being used *in situ*, without isolation [475, 476].

9.2.2 Coupling reactions

General. The palladium-catalyzed cross-coupling of organotins with various molecules bearing electrophilic carbon centers has received considerable interest during the last few years. Its many applications have their origin in the work of Migita [477], which has been considerably developed by Stille [478]. It is most often referred to as the Stille reaction. This topic has been recently reviewed [479–482].



Usually, only one organic group from the tin is transferred, as triorganotin halides are quite unreactive under these conditions. However, coupling of trichloroorganotins with aryl halides in water, leading to inorganic tin residue, has recently been carried out [483, 484]. Among organotins, the order of reactivity follows the sequence alkynyl > vinyl > aryl > heteroalkyl > alkyl, which explains why organotributyltins or organotrimethyltins are good substrates in this reaction, the more reactive fourth group being transferred first. The more common organic partners are halides and triflates which can be prepared in several ways and which can be obtained in the given configuration.

The fact that the Stille reaction is effective in the presence of a wide array of functional groups, including alcohol [485], halide [485], epoxide [486], primary [487–490] or quaternized [491] amine, the nitro group [485], aldehyde [492–495], ketone [485], ester [485], organic acid [483, 484, 496–500], primary amide [501], amine oxide [502] and sulfoxide [503–505], on either the organic or the organo-metallic substrate, and that it is a stereoselective coupling, is the reason for its success and led to the wide development of its applications. As the reaction conditions are often reactant dependent, it is difficult to give any general conditions for successful Stille couplings. The statement that ‘the choice of catalyst can provide headaches’ is still topical and can be extended to the choice of cocatalyst(s) and solvent [479]. The real catalyst of the reaction seems to be bis(triphenylphosphine)palladium, formed after reduction by the organotin, when the reaction is conducted either with dichlorobis(triphenylphosphine)palladium, benzylchlorobis(triphenylphosphine)palladium or tetrakis(triphenylphosphine)palladium. Many types of solvent can be used, from chloroform to dimethylformamide. Polar solvents increase the rate of transmetallation but seem to decrease the stability of the catalyst. Important recent improvements in the coupling were the discovery of the importance of both the nature of the ligand in the catalyst and the use of copper salts as cocatalysts. Ligands such as tri(2-furyl)phosphine or triphenylarsine, which are less donating than the popular triphenylphosphine, were found to increase coupling rates in allowing a faster transmetallation resulting from the easier dissociation of ligand [506, 507]. Copper salts, especially the iodide, speed up coupling reactions between vinyltins and tosylates [508] or iodides [509], probably via an extra transmetallation step involving organocopper intermediates [467] and are now common additives for sluggish Stille couplings. Intramolecular assistance either at tin [510, 511] or palladium [512] by a nitrogen atom enhances the rates of coupling. It allows selective alkyl [510], aryl [511] or vinyl [512] group transfer from the tin to organic halides and even usually unreactive aryl chlorides. To lower the cost of the Stille reaction, traditional soluble palladium catalysts can be replaced by inexpensive palladium on carbon. With copper iodide as catalyst and triphenylarsine as ligand, good coupling yields are obtained in this reaction, which is probably of a heterogeneous nature [513].

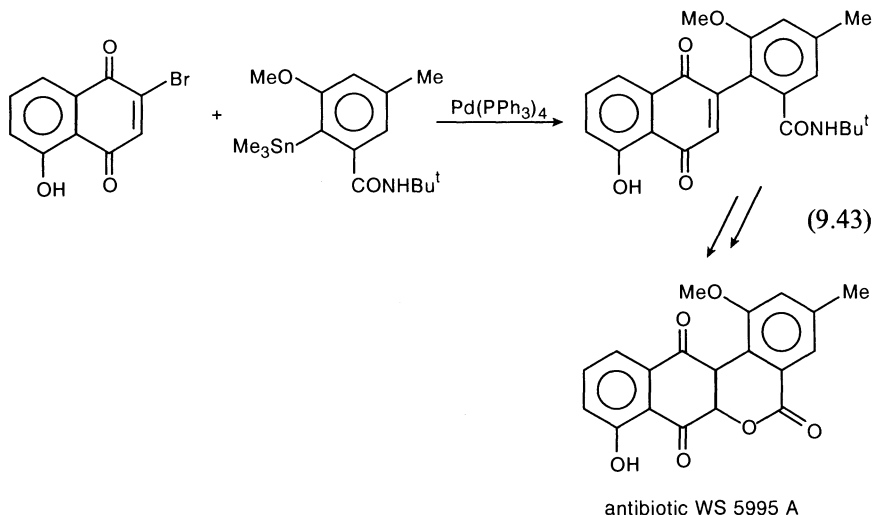
The more commonly encountered side reactions are alkyl transfer from organotrialkyltin [514, 515] and homocoupling arising from either organotin [516, 517] or electrophile [515]. Homocoupling products are the only reaction products where the electrophilic partner is omitted [518]. Steric effects, which slow down the desired process and allow side reactions to compete with it, can affect the yield of coupling product with (*Z*)-alkenyltrialkyltins [494, 515] or with *ortho*-disubstituted aryltins [519]. Tributyltin chloride formed in the reaction can act as a reducing agent with unsaturated acyl chlorides [520]. In some cases, i.e. for hindered vinyltins, *cine*-substitution is the main pathway of the reaction [521–523], which was explained by a competitive process involving a palladium carbene intermediate [522]. Transfers of aryl groups of the phos-

phine ligand to organic halides can be predominant, especially with less reactive electron-rich aryl halides [524, 525].

The interest of industrial chemists in the Stille reaction has led to studies designed to achieve easier recovery and purification of the products. This goal was achieved in the synthesis of biaryls [526, 527] or 1,4-benzodiazepines [528] attaching either aryl halides [526, 527] or aryltins [527, 528] to an amide resin. Polymer-supported tin reagents allow a reduction of the amount of tin residues in the organic target molecules [529].

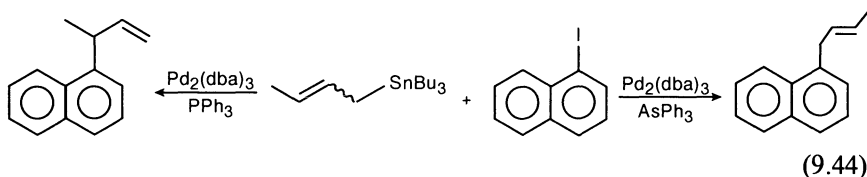
Organotins. Comprehensive studies have been conducted with aryl triflates, halides and various organotin reagents. Acyclic and cyclic 2-carbomethoxyethyl enol triflates derived from acetoacetates are coupled with tin reagents with good yields using, in the first case, tetrakis(triphenylarsine)palladium and copper iodide in NMP [530] and, in the second one, palladium acetate and triphenylphosphine [531] to give substituted 2-alkenoic esters of the terpene [530] or cephalosporin type [532]. A free *ortho*-hydroxyl group in a triflate does not interfere in the coupling of organotins and triflate-substituted anthraquinones [533]. Hindered, electron-rich phenol triflates couple with vinyltins when triphenylphosphine is used as a ligand and when larger than usual amounts of palladium are employed (10–15%) [534]. Arenesulfonates, which are cheaper and more stable reagents than triflates, can be used instead [535].

Coupled with various tin reagents, halogen-substituted heterocycles such as 6-halopurines [536], 5-bromopyridines [537], α -halolactams [538] or 2-bromoquinones give the corresponding heterocycles, which include the alkaloids nauclefine, angustine, nauclefine [537] or antibiotics WS 5995 A and C [539].



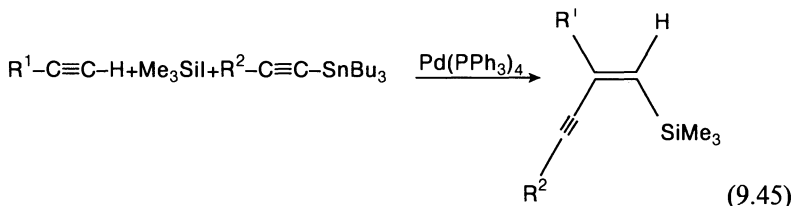
Alkyl-, allyl- and acylorganotins. Only a few studies deal with simple alkyl-,

allyl- or acyltins. Alkyl group transfer from tetraalkyltins allows an easy alkylation at C-8 of brominated adenosine analogues, under palladium catalysis [540]. Tetrazolyl or pseudo-saccharyl *O*-ethers of phenols, easy to purify, provide alternative leaving groups to triflates for cross-coupling reactions [541]. A crotyl group can be stereospecifically grafted to aryl iodides to give either the branched isomer when triphenylphosphine is used, or the linear isomer with triphenylarsine [542].



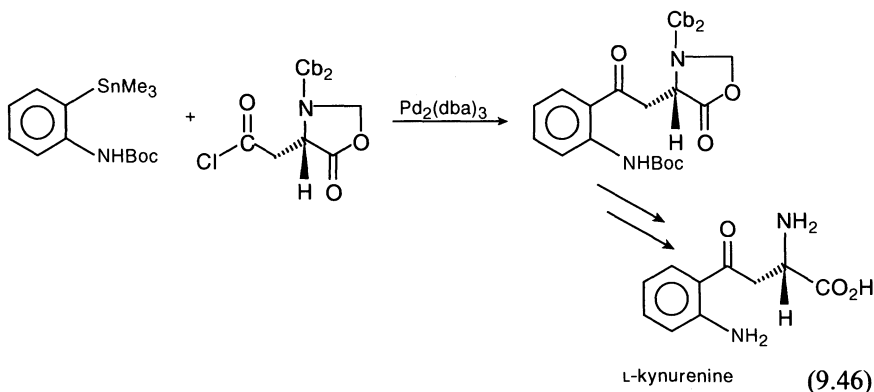
Carbamoylstannanes have been shown to transfer selectively carbamoyl groups to aryl or vinyl halides to produce good yields of aroyl and alkenoyl amides [543]. While benzyltrialkyltins are known to react with acyl chlorides with inversion of configuration [472], the same reaction conducted with chiral 1-(benzoyloxy)octyltin leads to retention of configuration [544].

Alkynylorganotin. Substitution of aryl [545], vinyl [546–550] and oxazolyl [551] halides and alkenyl(phenyl)iodonium triflates [552] with alkynyltins is a selective reaction which occurs successfully with both functional alkynyltins and functional halides. In the presence of an aryl triflate group, selective alkynylation at aryl bromine is observed when the cocatalyst LiCl is excluded [545]. Symmetrical dialkynyl imines are obtained via the coupling of ethynyltins with isocyanide dichlorides [553]. Stepwise dialkynylation of *N*-phenyl phenylthioimidoyl chloride gives unsymmetrical dialkynylimines provided that the first step is catalyzed by dichloro[1,1-bis(diphenylphosphino)ferrocene]palladium [554]. It is also possible to couple alkynyltins with vinyl halides generated *in situ* by the addition of trimethylsilyl iodide [555] or allyl chlorides [556] to alkynes. The reaction can be conducted under either palladium [555] or nickel [556] catalysis and gives conjugated (*Z*)-enynes.



Arylorganotin. The coupling of aryltins is very effective with heteroaryl triflates, even with a free amino group in the *ortho* position from tin. Analogous bromides also undergo the same reaction, although the corresponding chlorides or mesylates did not give such good results [514]. Phenyltin couples with vinyl bromides generated *in situ* by addition of aryl bromides to nor-

bornadienes. It leads to 2,3-diarylnorbornenes [557]. With 4-chloro-2-cyclobutenones, in a carbon monoxide atmosphere, a ring enlargement occurs during the reaction, which leads to 6-arylpyrones [558].

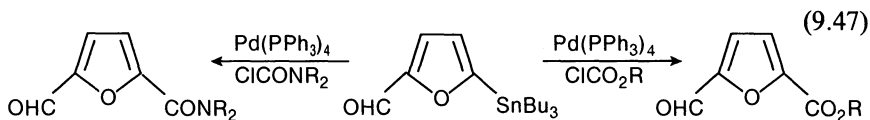


The aromatic amino acid kynurenine is easily prepared by the palladium-catalyzed reaction of an *ortho*-substituted aryltin with a functional acyl chloride [559]. Interestingly, triaryl tin halides can be involved in the Stille reaction although these halides are usually considered as unreactive. When fluorotriphenyltin is transformed into tetrabutylammonium difluorotriphenyltin, the tin-phenyl bonds are activated, allowing a smooth coupling to occur with alkenyltriflates [560].

Cyclic heterosubstituted organotins. The presence of an α -heteroatom, either oxygen or sulfur, in alkyl- or alkenyltins lowers the stability of the corresponding tin-carbon bond which allows a smooth transfer in Stille reaction conditions. The anticancer agent (+)-goniofufurone is obtained from the palladium-catalyzed coupling of a bicyclic glycosyltin and benzoyl chloride which occurs with retention of configuration at carbon. Cocatalysis by copper cyanide is required for optimum results [561], as with stannyl pyranosides [562].

Introduction of a glycol ring in the synthesis of leukotriene B_4 is achieved by the reaction of a stannyl glycol with an alkynyl bromide [563]. Aryl iodides are also able to couple [564], even in the presence of a free *ortho*-hydroxylmethyl group [565], as can acyl chlorides [566–568].

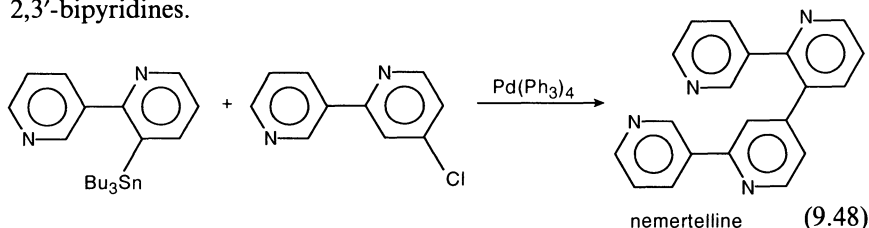
2-Furanic or 2-pyrrolic esters or amides, where the ring is substituted by a formyl group in either the 3-, 4- or 5-position, are obtained when the corresponding 2-stannyl heterocycles are treated by either chloroformates or carbamoyl chlorides, in the presence of a palladium complex [492].



Cycloaddition of alkynyltins and nitrile oxides gives 5-stannylisoxazoles which are able to undergo classical Stille chemistry [569]. With 2-substituted aryl halides, opening of the heterocycle followed by cyclization leads conveniently to quinolinones [570] or quinolines [571] from 2-nitrobromobenzene, and chromones from 2-(methoxymethoxy)bromobenzene [570, 572].

2-Stannylindoles are good substrates in Stille reactions provided that the nitrogen is protected by either a [2-(trimethylsilyl)ethoxy]methyl [495, 573] or a carboxyl [574] group. The BOC protecting group decreases the activity towards coupling [495]. Acyl formyl chlorides give better results than acyl chlorides in the synthesis of 2- and 4-acylpyrimidines from the corresponding tin reagent [575]. The key step in the preparation of lavendamicin [576] and streptonigrin [577] analogues consists of the coupling of 2-stannylquinoline with 2-chloro-3,4,5,6-tetrasubstituted pyridine. 4-Stannylloxazoles are useful in the synthesis of unsymmetrical 2,4-bis-oxazole, by coupling with 2-iodooxazoles, under palladium catalysis [578], in the preparation of hennoxazole A.

Previous examples were related to stannylated heterocycles where the tin is close to a heteroatom. A more remote position of the tin from the heteroatom, which could induce a lower reactivity of the metal-carbon bond, also allows very successful coupling. Two bipyridine components of nemerteline were obtained using a Stille reaction between substituted 4-chloro- and 3-stannyl-2,3'-bipyridines.



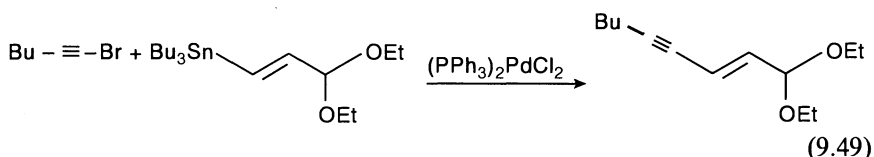
This hetaryl chloride is active in coupling although bromides are usually preferred [579], as when 4-stannylpyridines are reacted with *ortho*-bromoacetanilides [580] or polyaryl bromides [581]. 5-Stannylpyrimidines are also good substrates: they give good yields of coupling products with aryl or vinyl bromides [582, 583]. The selective and straightforward synthesis of regiospecifically *N*-oxidized or *N*-quaternized polyazine was achieved for the first time by the coupling of *N*-oxidized or *N*-quaternized hetaryl tins with hetaryl halides, including chlorides, or by the coupling of hetaryl tins with *N*-oxidized hetaryl bromides [502], under palladium catalysis [491]. 3-Stannylfurans are good precursors of 3-acyl- [584, 585] or aryl- [493] furans which have been used in a short synthesis of Perilla ketone [584] and in a highly efficient preparation of manoalide [585].

Vinylorganotin. The preparation of multisubstituted alkenes of a given configuration is still an important challenge in organic chemistry. As vinyltins

are easily prepared stereospecifically with either one, two or three [586–588] substituents on the double bond, they are commonly involved in the preparation of alkenes. These studies represent about half of the applications of the Stille reaction in the last decade.

Halides. Allethron, an allylcyclopentenone is conveniently obtained from the coupling of an α -stannylated cycloenone with allyl chloride in the presence of dibenzylacetone palladium [589]. When the allyl chain is substituted by a methyl group, the coupling is also successful in the synthesis of tetrasubstituted quinones [588] from trisubstituted stannyl quinones. With a methyl and an alkoxy group, it allows a rapid synthesis of the mycotoxins monocillin I and monorden [590], and of 11, *O*(3)-dihydropseudopterolide [591]. The same reaction was used to vinylate 3-bromo-2-cyclopentenone, without migration of the double bond. In this process, (*Z*)-vinyltins are more inclined to homo-coupling than (*E*) isomers, which is nevertheless a minor reaction [592]. Bromoalkynes are good substrates in the Stille reaction, which leads to functional enynes with functional vinyltins. As above (*Z*)-vinyltins give slightly reduced yields with respect to (*E*)-vinyltins [593].

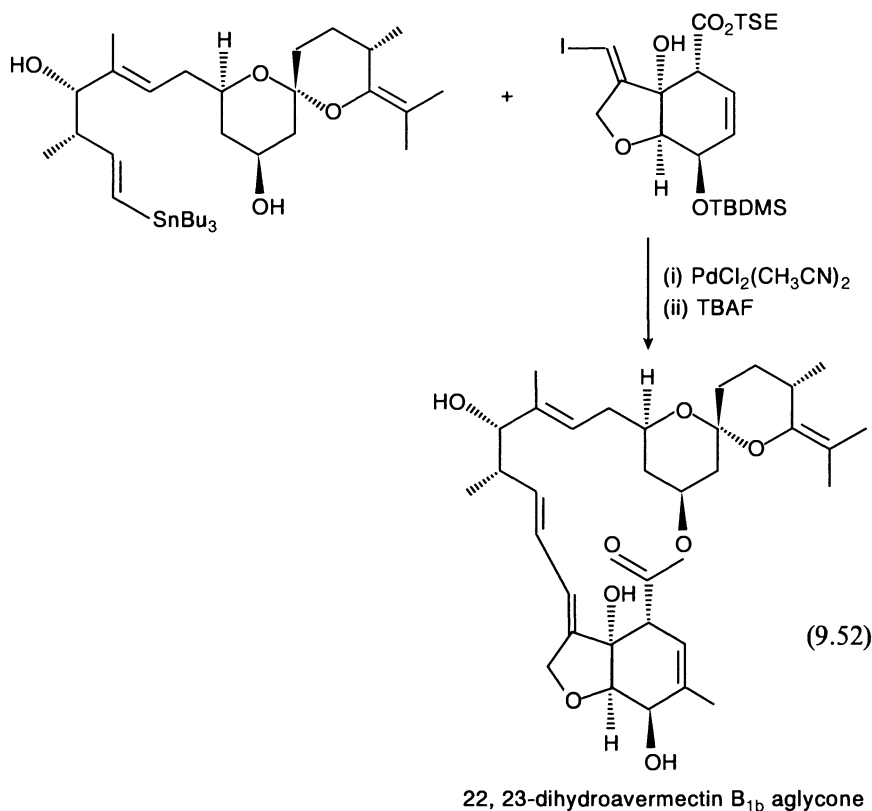
p-Substituted aryl bromides are originally found to undergo coupling with vinyltin [594] to give functional styrenes. This reaction has been extended to functional vinyltins with (*E*)- [595] or (*Z*)-substituted double bonds [596]. In the latter case, electron-donating substituents such as primary amino or hydroxyl groups retard the reaction completely. However, protection of these groups relieves this effect.



Acrylates or acrylic ketones, substituted by tin either at the 2- or 3-position, have been extensively used in the coupling with aryl iodides and are often performed in the presence of catalytic amounts of copper iodide for easier transmetallation. Previous unsuccessful coupling of trisubstituted (*E*)-2-stannylacrylates with aryl iodides were carried out in the presence of 0.7 equivalents of copper iodide, to give (*E*)-2-arylacrylates in good yields [597]. (*Z*)-substitution of the double bond does not prevent the coupling, which occurs with total specificity [598]. When the acrylate is included in a cycle, as in 2- or 3-(5*H*)-stannylfuranones [599] or 3-stannyltetronates [600], aryl iodides and acyl chlorides also couple, despite the lower reactivity of the 2-stannyl isomer. As mentioned above, high substitution of double bonds does not hamper Stille couplings. Tetrasubstituted (*Z*)-3-stannyl-2-alkenones undergo smooth coupling with aryl iodides to give tetrasubstituted (*Z*)-3-aryl acrylates in the presence of palladium complexes and copper iodide, provided

Enantiopure dienyl sulfoxides are available by virtue of Stille coupling. This methodology gives various 1-sulfinyldienes of given configuration from (*Z*)- or (*E*)-halovinyl sulfoxides and vinylstannanes, bromides and iodides with equally good results [504]. The coupling is only effective when conducted in the presence of 1 equivalent of radical inhibitor [505]. It is also possible to prepare dienyl amines in this way provided that the amino group is not a primary amine. The amino group can be linked to either the organotin [606, 607] compound or the halide [608, 609], which gives a high flexibility to this method, particularly useful for the synthesis of modified amino acids from iodoallylglycinates [609]. As vinyl iodides are readily available from aldehydes, their coupling with stannylallylic amines provides an efficient stereospecific four-carbon homologation of aldehydes to dienamines [606].

Dienyl systems are often present in natural products. Stille coupling is particularly useful in the synthesis of the aglycone of 22,23-dihydro-avermectin B_{1b} to build a dienyl unit from a vinyltin and a vinyl iodide, which both bear unprotected hydroxyl groups in either allylic or homoallylic positions [610].

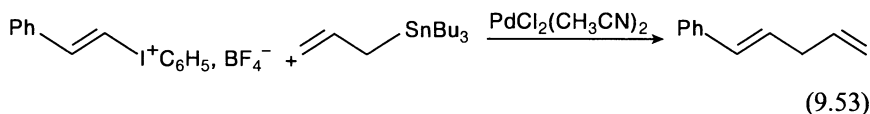


A one-pot reaction of iodoandrostene, vinyltins and functionalized alkenes allows an easy synthesis of a polycyclic androstane-based skeleton [611] by coupling followed by Diels–Alder reaction.

α -Substitution by a carbonyl enhances the reactivity of vinyl halides. This allows an easier oxidative addition to palladium, which makes the use of iodides unnecessary to obtain high yields of coupling products. Bromides and chlorides can be used as well. α -Bromo- [612], α -iodoenones [613] or α -iodoacrylates [614] couple well with vinyltins under palladium catalysis to give dienones or dienic esters, which are key intermediates in the synthesis of the fully functionalized core of zaragozic acid [612] or miroestrol [614]. The presence of copper iodide promotes the reaction of stannylcyclobutenediones with 3-chloro-3-cyclobutene-1,2-diones, which are as reactive as the corresponding bromides, even in the presence of a free primary amino group [489].

α -Chloroheterocycles belong to another class of activated halides where the halogen can undergo an easy substitution reaction. That is indeed the case with 1-chloro- β -carbolin [615], 6-chloropurines [616] and 2,6-dichloropurines, where the usually more reactive 6-chlorine is also the more reactive in the Stille reaction. Selective vinylation with vinyltins in the 6-position is possible, leaving the 2-chlorine unchanged. However, phenyltin does not give such selective results [617].

The reactivity of hypervalent iodine in alkenylphenyl iodonium salts is usually higher than that of normal iodine. This is also the case in the Stille reaction where the coupling of iodonium salts with vinyltins is reported to be very fast, even at room temperature, the easier insertion of palladium in the carbon–iodine bond allowing mild conditions [618].

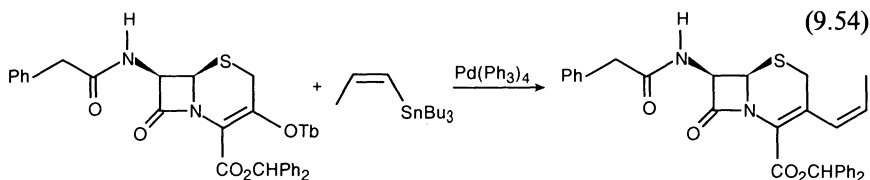


The same palladium catalyst can be used in a one-pot procedure to promote two different reactions: first, addition of a vinylic organic halide on an activated alkene such as norbornadiene and then coupling of the halide formed *in situ* with a vinyltin reagent. This method provides an interesting entry to 1,5-dienyl compounds where unprotected substituents such as hydroxyl, keto or ester groups can be involved [619].

Triflates. Dienynes of a given geometry are obtained in the reactions of triflates derived from β -ketoesters and enynylnyltins, under palladium catalysis, while the corresponding iodides give very poor results. Both fluorosulfonates and triflates react in this coupling [620]. The Stille reaction is successfully applied to the synthesis of austalide B with a triflate derived from a lactone [621]. The grafting of an acrylamide group on a benzodiazepine framework allows the synthesis of anthramycin through a pyrrolyl triflate. A free amide

attached to the organometallic substrate did not prevent the reaction from occurring [501]. β -Stannyl- α,β -unsaturated ketone or Boc-protected amine allows easy access to quinolones by reaction with quinolyl triflates [622]. Copper iodide is necessary to couple allenyltins with aryl triflates under palladium catalysis, otherwise yields of arylallenes are very low even in the presence of triphenylarsine [623]. Mesylates [624] can be used in addition to fluorosulfonates [620, 625] in the Stille reaction as shown in the coupling of β -methanesulfonyloxyl enones with vinyltins under palladium catalysis. Given that stoichiometric amounts of lithium bromide are necessary, β -bromo enones are probably formed *in situ* [624]. As mesylates are often more stable than triflates [626] this reaction can be quite convenient. However, only reactive tins couple, aryltins giving low yields.

The presence of an α -amino acid protected as an amide and an ester on a vinyltin does not prevent the coupling from occurring with triflates, even with hydroxy-substituted ones. This reaction allows the formation of the side chain of unnatural α -amino acids [523]. The Stille reaction is found to be very versatile in cephalosporin chemistry, where its exceptionally mild conditions allow the general introduction of unsaturated substituents at C-3 from the corresponding triflate and vinyltins, under palladium catalysis [627, 628].

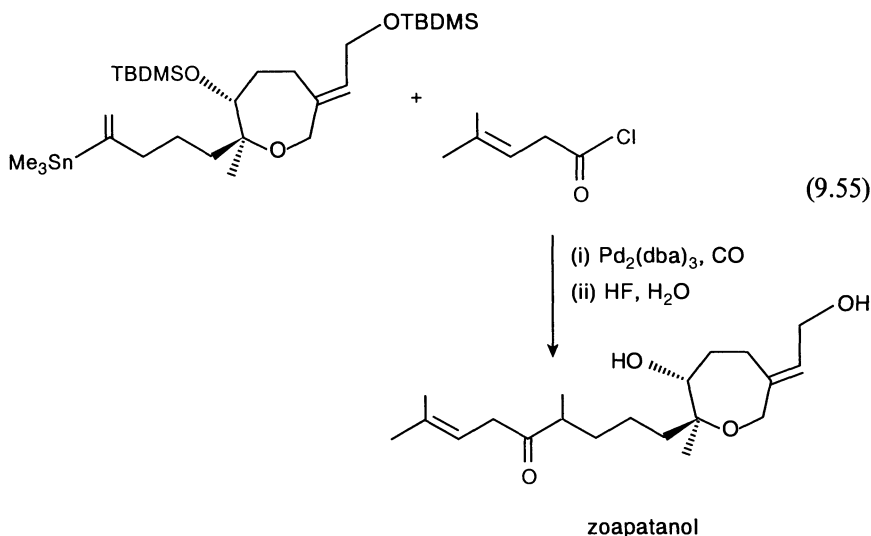


Dienyl pyranosides, useful starting materials for the synthesis of natural products, are prepared from enol triflate pyranoses and vinyltins with tetrakis(triphenylphosphine)palladium as catalyst and lithium chloride as coreactant [629].

Acyl chlorides. The first couplings of tin reagents under palladium catalysis were achieved with acyl chlorides, and applications of this reaction received considerable attention during the first decade after its discovery. However, examination of the literature covered by this review revealed that interest in this method of preparation of ketones decreased slightly. It was used with 3-methoxyalkenyltins and acyl chlorides to give either conjugated or non-coupling products, depending on the solvent employed. Further hydrolysis gave β -acylpropionaldehydes [630]. The introduction of 1,1,1-trifluoropropen-2-yl groups was possible by using 1,1,1-trifluoropropen-2-yltin and acyl chlorides under palladium catalysis. It has been applied in steroidal chemistry [631]. As in other coupling reactions, stannylated esters and ketones are valuable substrates. This is shown by the reaction of 3-stannyl-

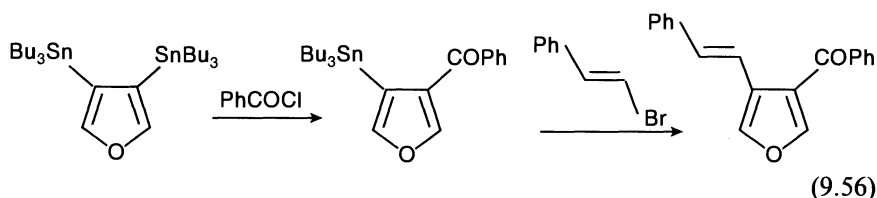
ated tetronic acids which are cleanly acylated., furnishing 3-acyl tetronic acids in the presence of a palladium catalyst and under a CO atmosphere to avoid decarbonylation [632]. In order to obtain good yields of 1,2,4-triketones, it is better to carry out the acylation of stannylcyclobutenedione in the presence of copper iodide as cocatalyst [633]. When the dienyl unit of a (*Z*)-dienyltin is protected with a tricarbonyl iron group, the coupling is not disturbed by the presence of the protecting group which was unchanged after reaction [634]. The Stille reaction is not limited to acyl chlorides. Chloroformates and carbamoyl chlorides can also be used to give α,β -unsaturated esters and amides [635]. Sulfonyl chlorides are also good partners in coupling, thus providing an easy entry to sulfones [496].

As the carbonylative coupling of tin reagents and halides results in ketones, it has been added to this section. This process has proved its versatility in the key step of a synthesis of strychnine, in which a vinyltin is coupled with an *ortho*-iodoaniline to give a bicyclic ketone [636], and in the last step of a synthesis of zoapatanol in which a vinyltin allows the introduction of a 1-oxo-3-pentenyl side chain [637].



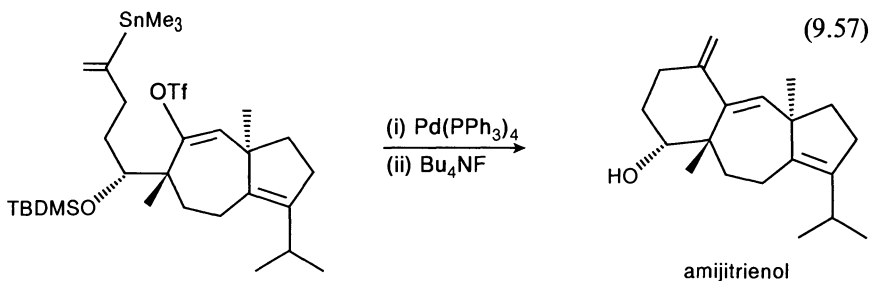
Symmetrical bis(organostannyl) compounds. It is worth mentioning the versatility of the Stille reaction in the selective preparation of symmetrically or, interestingly, disymmetrically substituted compounds from symmetrical bis(organostannyl) compounds where one or both tin-carbon bonds can be selectively cleaved. Symmetrical or unsymmetrical 1,4-diketones are obtained from 1,2-distannyethene and acyl chlorides [520]. From the same tin compound, coupling with aryl bromides followed by cleavage of the second tin by bromine leads to β -bromostyrenes [638]. Further separation of both tins by an ethylene unit in 1,4-distannylbutadiene allows the same selectivity

[639]. Both tins in 3,4-distannylated furans are easily discriminated in the Stille reaction, as the replacement of a tin by an acyl group lowers the reactivity of the second one. Further reaction with halides and bromine gives 3,4-unsymmetrically substituted furans [640].



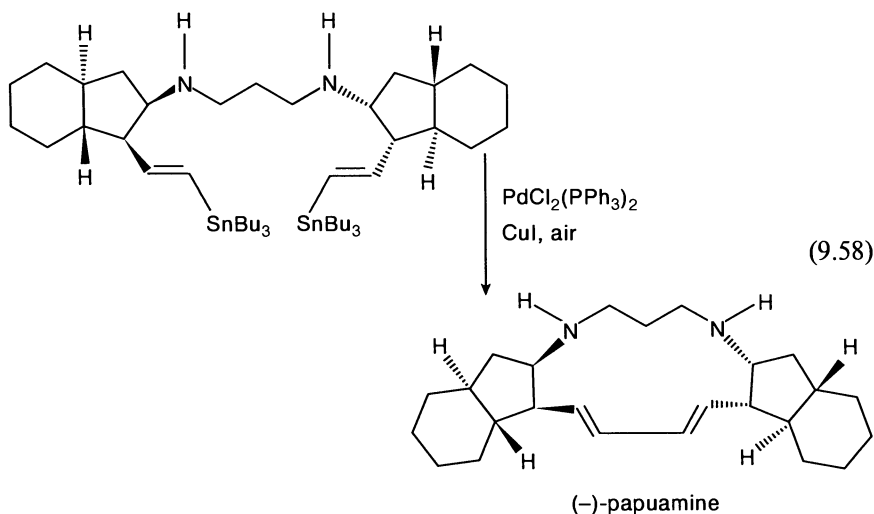
Stepwise acylation of bis(trimethylstannyl)pyridines [641] and pyrimidine [575] is a good method of preparing unsymmetrical diacylpyridines and pyrimidines as several isomers of the starting tin compounds are easily available.

Cyclization reactions. An important feature of the Stille reaction, revealed only recently but giving rise to rich and new chemistry, lies in its application in cyclization processes. Early examples were described under high dilution [642] but it was soon shown that special conditions (dilution, syringe-driven additions) typically used in annulation chemistry are not necessary to obtain good results. Furthermore this reaction is not limited to thermodynamically favored five- or six-membered rings but can be applied to the construction of cycles with four to 29 members! Another interesting characteristic of this cyclization reaction is that it is also effective with distannylated compounds and disubstituted ditosylates or dihalides. Norpatulodide B is prepared by the cyclization of an intermediate terminating at one end with an acid chloride and at the other with a (*Z*)- β -stannylalkenoate, under palladium catalysis [643]. Stannyl chloroformates also undergo intramolecular coupling to provide a novel route to α -methylene lactones [644]. Vinyltriflates, which do not have to be isolated but can be generated *in situ*, cyclize in Stille conditions when they are substituted by an ω -vinyltin with either an internal or external double bond to give conjugated dienyl cycles. This scheme has been used in the synthesis of the diterpenoids amijitrienol, amphilectene [645] and dolastatrienol [646].



Methylene cyclobutanes [647] and benzocyclobutanes [648] can easily be reached using stannylvinyl halides, which are therefore as powerful agents as triflates. In preparing zearalenone, it is found that the cyclization of a carboxylic ester terminated at one end by a vinyltin and at the other by an aryl iodide is more efficient than with an aryltin and a vinyl iodide [649]. Aryltin-substituted aryl halides are generated *in situ* by treatment of a diaryl dihalide with a ditin in the presence of palladium catalyst. Further reaction leads to cyclized compounds such as hippadine [650].

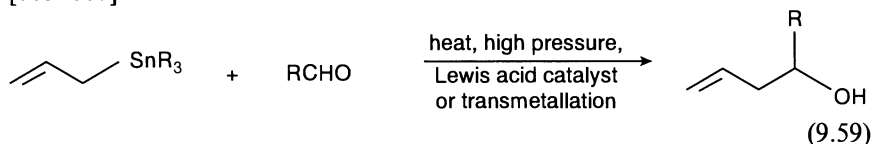
Rapamycin, a substituted 29-membered cycle, is prepared in two ways, involving either the cyclization of ω -(stannylvinyl)vinyl iodide [651] or the double reaction of an ω -diiodide with 1,2-distannylethylene [652]. With halides as substrates, either *trans*-, from an (*E*)-vinyltin [653, 654], or *cis*-annulation, from a (*Z*)-vinyltin [486, 655], can be successfully performed. Alkynyl- [656], allyl- [657], or benzyltins [658] and alkynyl [486] or allylic [659] halides can be used as well. Three independent syntheses of papuamine, a marine alkaloid, involve in the final step the creation of a 12-membered ring via Stille coupling of vinyltins [660–662].



9.2.3 Reactivity of allyl-, propargyl- and allenylorganotin

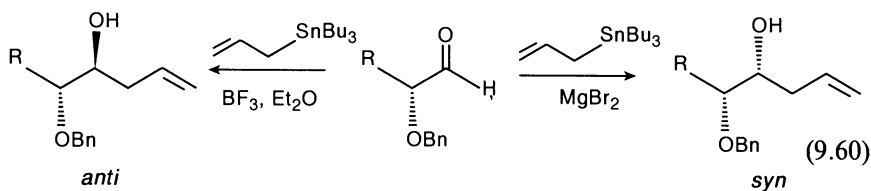
Selectivity is one of the more important goals of modern organic chemistry. From this point of view, allyltins are very important reagents which allow, mainly by their regio- and stereoselective addition to carbonyl compounds, the preparation of functional homoallylic alcohols with very efficient control of several stereogenic centers, far better than that observed with other allyl-metals. This reaction can also occur through several mechanisms in which the stereochemical course is different. Therefore, by varying the experimental

conditions or the nature of the catalyst, it is often possible to obtain stereospecifically couples of isomers. Another interesting feature is their high degree of chemoselectivity. They can thus be employed with many functionalities, often avoiding the use of protecting groups, which make them very useful reagents in organic chemistry. This topic has recently been reviewed [663–667].



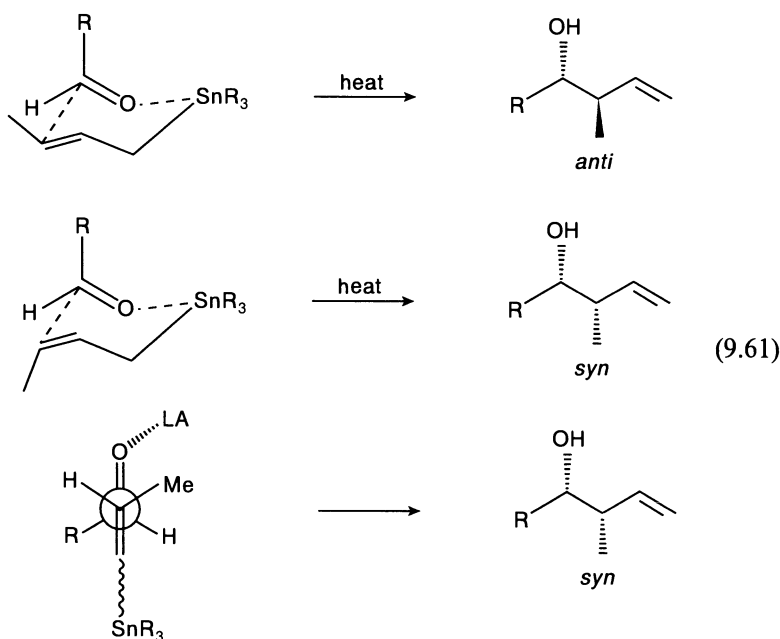
Allylorganotins. Simple allyltins can add to carbonyl compounds either thermally or with a Lewis acid as catalyst. Thermal additions, or additions promoted by high pressure [668, 669], have been proposed to proceed through a six-membered, chair-like transition state. Catalyzed reactions, which are used far more than thermal ones and usually give higher yields, proceed through acyclic transition states. The more common catalysts are boron trifluoride, titanium tetrachloride and magnesium chloride. Lewis acids as mild as silicon halides promote addition of allyltins to aldehydes; methyltrichlorosilane [670] can be used in non-polar solvents while trimethylchlorosilane only gives good results when it is used in acetonitrile [671]. A scandium derivative, scandium trifluoromethanesulfonate, allows the allylation of aldehydes and ketones in aqueous medium, which is an advantage with compounds which are difficult to dry, such as sugars or peptides [672]. Tetraallyltin in methanol is sufficiently reactive to enable addition to aldehydes without catalysts at room temperature [673]. Highly chemoselective allylation of aldehydes in the presence of ketones is allowed when the aldehyde is converted *in situ* into 1-silyloxysulfonium salts [674]. Enantioselective synthesis of homoallylic alcohols is possible by using an inductive group as a chiral sulfoxide in the β -position to the carbonyl. High enantiomeric excess is recorded (94% *ee*) [675]. Equally good results are recorded with ketones substituted by a chiral π -allyltricarboxyliron group [676]. It is also possible to use a chiral catalyst prepared from a Lewis acid and an optically active ligand. This procedure gives very high enantiomeric excess with (+)-binaphthol as ligand (>95% *ee*) [677, 678]. Non-linear effects have been observed where a catalyst of 50% *ee* yields a product of 88% *ee* [679].

Substituted aldehydes can react with two addition paths giving *syn* or *anti*-[680] adducts. The stereochemical course of the reaction depends on the presence or absence of a catalyst and, if a catalyst is added, on whether chelation occurs between aldehydes, substituent and catalyst. With α -alkoxyaldehydes, when chelation is possible, as with TiCl_4 , MgBr_2 [681] or LiClO_4 [682, 683], the conformation of the complex induces the formation of a *syn* adduct by nucleophilic attack opposite to the alkyl substituent. When it is not possible, as with $\text{BF}_3\text{-Et}_2\text{O}$, an *anti* adduct is obtained.



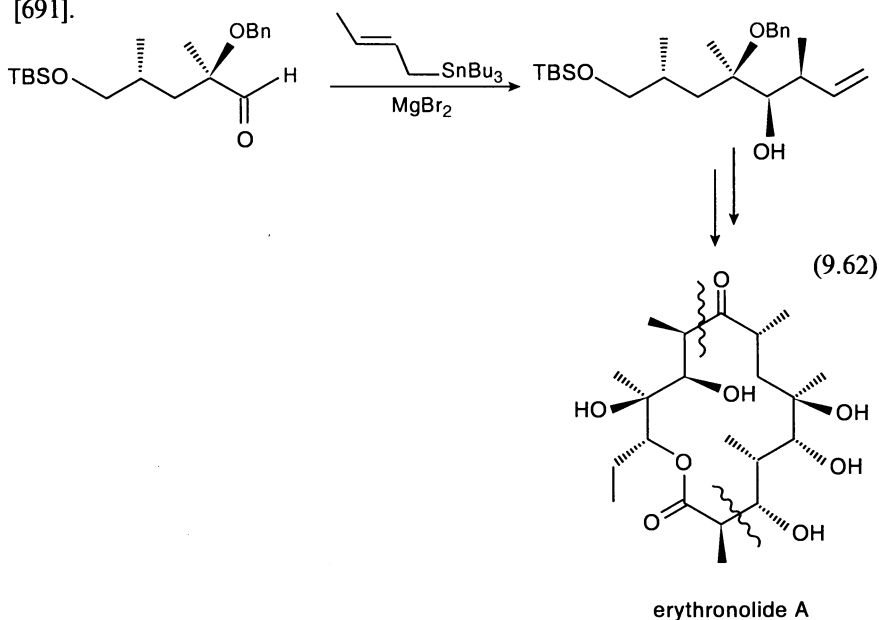
The stereoselectivity is reversed when the complexing group is located one carbon further from the carbonyl. β -Alkoxyaldehydes [684] lead to *anti* addition with MgBr_2 , and with α -alkyl- β -alkoxyaldehydes [685] and $\text{BF}_3\text{--Et}_2\text{O}$ the stereochemistry is governed by the more remote alkoxy center: *syn* addition with respect to this center is observed regardless of the configuration of the α -alkyl group. When a good leaving group such as a bromide or a chloride is present near the carbonyl of a ketone, elimination of tin halide occurs in the tin alkoxide intermediate formed by the addition of the allyltin, leading to an allylated epoxide [686].

*(2-Propenyl)organotin*s. With substituted allyltins, especially crotyltins, α - or γ -adducts can be formed. If γ -adducts are preferred, two diastereomers are possible. If addition leads to α -adducts, the configuration of the double bond can be either (*E*) or (*Z*). γ -Adducts are usually formed and, when the reaction is performed under heating or under high pressure [666, 668] *anti* diastereomers are obtained from (*E*)-organotinins while *syn* diastereomers are formed from (*Z*)-organotinins.



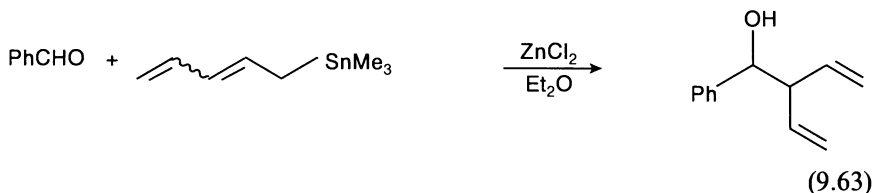
However, double substitution in the α - and γ -positions and thermal conditions induce *anti* (*Z*)-additions [687]. In the presence of a Lewis acid, when transmetallation is not achieved, *syn* diastereoselectivity is observed from either (*E*)- or (*Z*)-isomers. Exceptions are possible, however, as with ZnCl_2 in DMF, where a selectivity analogous to that of thermal reactions and dependent on the configuration of the starting organotin is explained by the occurrence of a cyclic transition state [688]. Platinum catalysts can also be used: they do not give any diastereoselectivity [689].

Three diastereoisomeric centers are formed with α -substituted aldehydes. When a chelating Lewis acid such as MgBr_2 promotes the addition to α -alkoxyaldehydes, *syn-syn* addition [690–692] is observed with crotyltin while *anti-syn* addition is reported with β -methylcrotyltin [690, 692]. This reaction was used in a stereocontrolled synthesis of erythronolides A and B [691].



The presence of α -methyl and β -alkoxy groups as substituents of the aldehyde induces a reversal of the selectivity with the same catalyst: *syn-anti* addition is observed. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ promotes a *syn-syn* addition with the same reagents [692, 693], which gives easy access to oligomycin B [693]. When the allyltin is substituted both at the α - and β -position, addition to dimethylglutaric hemialdehyde is dependent on the position of the γ -methyl of the aldehyde: the *meso*-aldehyde (*syn*-methyls) gives an *anti-syn* adduct while the (\pm)-aldehyde (*anti*-methyls) produces a *syn-syn* adduct [694]. A chiral binaphthol-derived titanium complex used as catalyst induces the formation of a *syn* adduct with high enantiomeric excess (86% *ee*) in the reaction between crotyltributyltin and methyl glyoxalate [695].

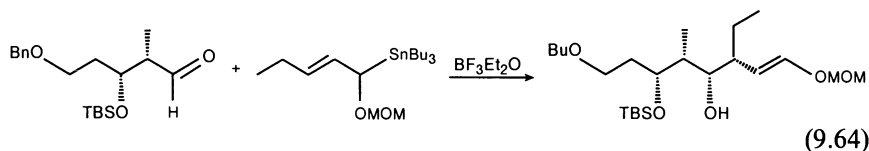
Pentadienyltins, which could give either α -, γ - or ϵ -adducts, yield only γ -products when the reaction is conducted in diethyl ether with ZnCl_2 as catalyst. The more common CH_2Cl_2 gives poorer selectivity [696].



Enoxysilanes also react with allyltins in the presence of Lewis acids to lead mainly to α -adducts [697].

(*Alkoxy-2-propenyl*)organotin. Easy and highly enantioselective synthesis of α - and γ -alkoxyallyltins has allowed considerable development in the enantioselective synthesis of open-chain substituted diols. These organotin add to aldehydes with transposition, either thermally or under catalysis with Lewis acids, giving a good method of synthesizing 1-alkoxy-1-buten-4-ols and 3-butene-1,2-diols, respectively.

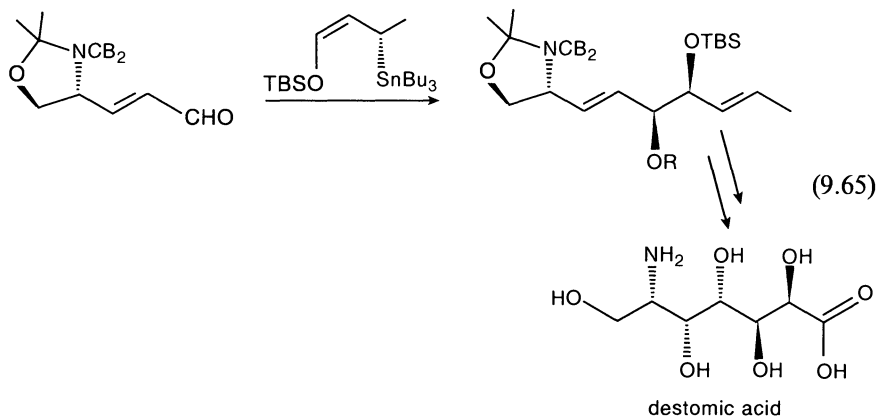
α -Alkoxyallyltins give (*Z*)-*anti* adducts with aldehydes under thermal activation [698]. With a chiral alkoxy group, diastereoisomeric allyltins can be prepared easily in pure form. Heated with chiral aldehydes, they yield adducts with very high *ee* values [699, 700]. Under $\text{BF}_3\text{-Et}_2\text{O}$ catalysis the selectivity is reversed: the same reaction gives (*E*)-*syn* compounds with very high *ee* values [701]. However, aromatic aldehydes induce (*Z*)-*syn* selectivity, which is explained by the different geometry of the aldehyde-Lewis acid complex [702]. Enantiomers of α -alkoxyallyltins lead to different enantioselectivities when they are opposed to chiral β -alkoxy- α -methyl aldehydes. The (*R*)-organotin gives the (*Z*)-*syn,syn* isomer while the (*S*)-organotin gives the (*E*)-*syn,syn* isomer. As one of the organotin enantiomers reacts faster than the other one, kinetic resolution allows the enantioselective synthesis of the (*E*)-*syn,syn* adduct from racemic organotin [703].



γ -Alkoxyallyltins can be obtained stereospecifically and enantioselectively in (*Z*) or (*E*) forms by isomerization from α -alkoxyallyltins [704, 705]. They lead, under $\text{BF}_3\text{-Et}_2\text{O}$ catalysis and with simple [706] or α,β -unsaturated

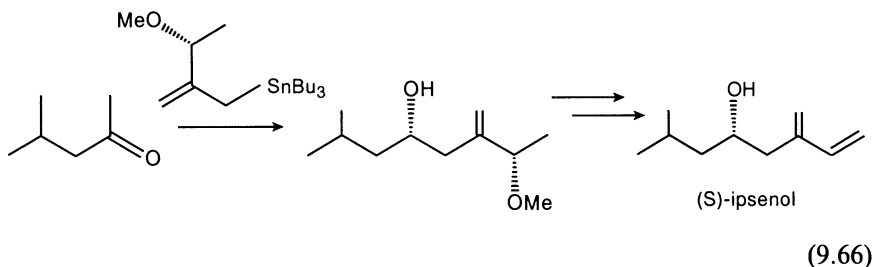
[707] aldehydes, to *syn*- α -alkoxy adducts from either (*E*) or (*Z*) [705, 706] allyltin starting compound. A chiral alkoxy auxiliary group induces the enantioselective creation of this *syn* carbon–carbon bond, giving chiral *syn*-diols after hydrolysis of the alkoxy group [708–710].

The center of chirality can be situated on the carbon linked to the tin. In this case, *syn*-condensation is also enantioselective when achiral aldehydes are used, readily available (*R*) and (*S*) organotins leading to couples of enantiomers with an (*E*) double bond. It was applied to the synthesis of (+)- and (–)-muricatacin [707] and of higher sugars [711]. With α -alkoxy- [710, 712] and α,β,γ -trialkoxyaldehydes [713], *syn,anti* adducts are obtained under $\text{BF}_3\text{--Et}_2\text{O}$ catalysis while MgBr_2 leads to *syn,syn* adducts with α -mono- [712, 714], α,β -di- [715] or α,β,γ -trialkoxyaldehydes [713, 716]. This MgBr_2 -induced addition allows an interesting entry into benzamide E [715]. Analogous selectivity is observed with protected α -aminoaldehydes [717]. When the amino group is separated from the carbonyl by a double bond, remote induction is as high as when the amino group is near to the carbonyl. This reaction was used in enantioselective syntheses of destomic acid and lincosamine [718].



The same reversal of selectivity that occurs with crotyltins is reported with β -alkoxy aldehydes, which leads to *syn,anti* adducts [719] under MgBr_2 catalysis.

β -(Silyloxymethyl), β -(acetoxymethyl) or β -(alkoxymethyl) groups on the allyl moiety do not interfere with the addition of allyltins to aldehydes. With simple aldehydes, the stereoselectivity of the reaction can be reversed by changing the alkoxy group: a methoxyl induces a *syn* addition while an acetoxyl gives preferentially an *anti* condensation. (*S*)-Ipsenol was prepared in this way with 70% *ee* [719]. In a synthesis of sesbanimide analogs, α -alkoxy aldehydes give *syn* adducts under catalysis with a titanium complex [720].



β -(Alkoxyethyl)pentadienyltins give preferentially ϵ -adducts with $\text{BF}_3\text{-Et}_2\text{O}$ and γ -adducts with TiCl_4 [721]. They have been used in a synthesis of (*R*)-7,11-dideoxydaunomycinone [722].

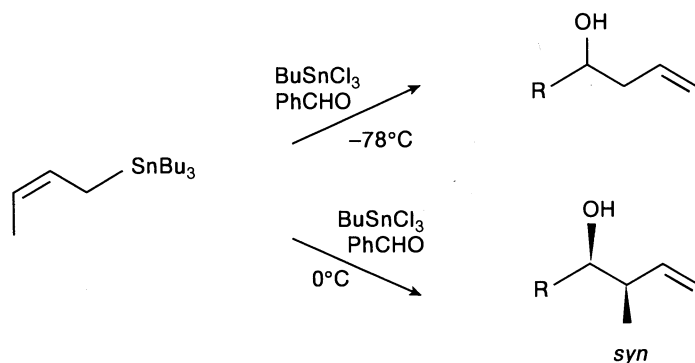
γ -(Alkoxyethyl)allyltins give interesting applications in organic synthesis. When the alkoxyethyl group is part of a sugar, these reagents are used in the synthesis of higher sugars [723]. With a more simple alkoxy group, acerosolide is prepared through a synthetic scheme involving both an allyltin condensation and a Stille coupling [724].

Haloallylorganotin and transmetallated reagents. The Lewis acid character of tin, when it bears chlorine atoms, allows its complexation by the carbonyl group of aldehydes. The acyclic transition state, which is accepted with allyltriorganotin under catalysis, is then changed into a cyclic six-membered one. This is also the case when transmetallation of allyltriorganotin is achieved with SnCl_4 , TiCl_4 or InCl_3 .

Simple chloroallyltins, prepared [725] or generated *in situ* from an allylic halide and SnCl_2 [726] give *anti* adducts with α -hydroxy aldehydes [725] and aldoses [726]. (*Z*)-Chlorocrotyltins react with aldehydes to give either linear (*Z*)-adducts [727] or *syn* α -substituted ones, depending on whether or not the reaction conditions [728] allow isomerization of the chlorocrotyltin generated *in situ*. (*E*)-Chlorocinnamyltins also lead either to the exclusive formation of linear (*Z*)-adducts or to the *anti*- α -substituted ones [729]. The reaction can be conducted in the presence of water, the linear regioisomer being obtained in the presence of an organic cosolvent, and the branched one with water alone [730]. Alcohols can be used with tin dihalides instead of allylic halides to prepare reactive crotyltins *in situ*, provided that a palladium catalyst is added (Scheme 9.2) [731].

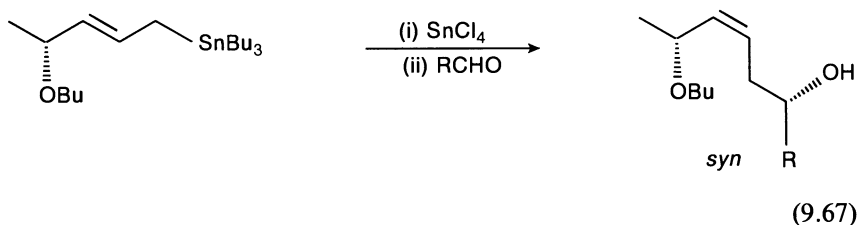
Substitution of the allyltin in the β -position by an alkoxyethyl group induces an *anti* addition to aldehydes [732] which leads to *anti*-1,4-diols after removal of the alkoxy group by hydrolysis. *In situ* generated β -carbomethoxyallyltins add to aldehydes and ketones to give methylenelactones in high yield. α -Substituted aldehydes lead to *syn* adducts [733].

A comprehensive study has been published of the reactivity of chloroallyltins, prepared *in situ* by transmetallation, substituted in δ - and/or ϵ -positions by alkoxy groups. From chiral δ - or ϵ -alkoxyallyltins, very high 1,5-



Scheme 9.2

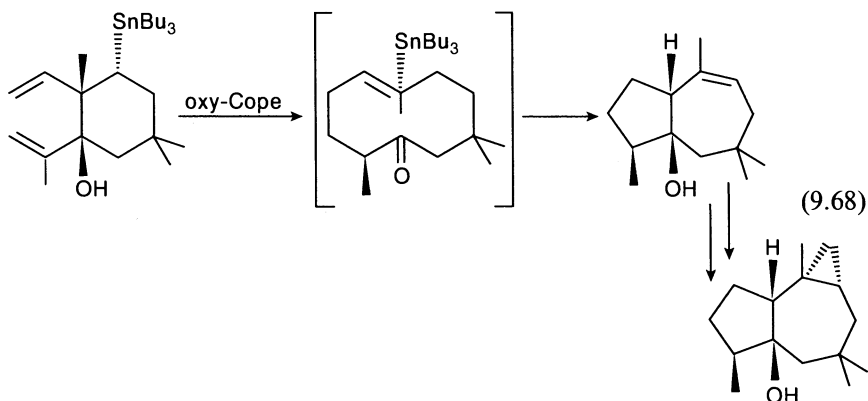
[734], 1,6- [735] or 1,7- [736] asymmetric induction is recorded in this preparation of chiral (*E*)-5-, (*E*)-6-, or (*E*)-7-alkoxyalken-2-ols. Alkoxy and hydroxyl groups are in a *syn* relationship. Chiral α -alkoxyaldehydes lead to *syn-anti* adducts [737]. The observed high stereoselectivity is explained by the occurrence of an internal coordination between the metal and the alkoxy group leading to four-, five- or six-membered cycles inducing very organized transition states [666].



Enantioselective preparation of homoallylic alcohols can be achieved by using chiral ligands on the tin. Allyltin tartrates lead to modest enantiomeric excess [738] while chiral diamines added to dibromodiallyltin give better results [739].

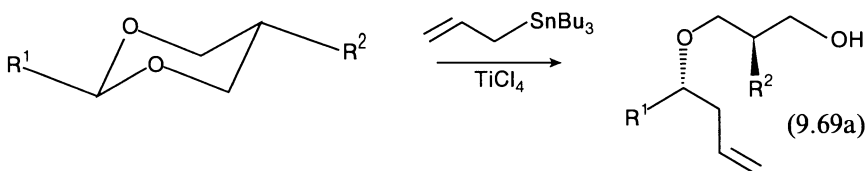
Cyclization reactions. Cyclizations can be achieved by the use of intramolecular additions of allyltins to aldehydes or ketones. In the process, the intramolecular pathway is highly favored compared to the intermolecular one, and thus heads the special techniques used to avoid intermolecular condensations. They have been used to build three- to 14-membered vinyl carbo- and heterocycles. Thus intramolecular condensation between allyltin moieties and the carbonyl group of aldehyde or ketone gives preferentially *anti* vinylcyclopropanols with ketones [740]. When the allyltin moiety and the carbonyl compound are already included in a cycle, a bicycle is formed. Such

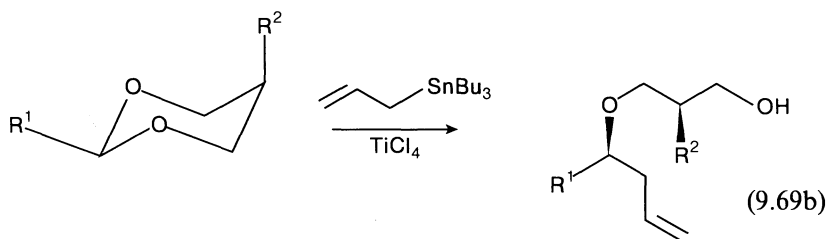
a reaction is used in a synthesis of africanol where the stereochemistry of the cyclization is controlled through the reaction conditions [741].



A cyclization is possible with α,β -unsaturated ketones through 1,4-addition: it leads to substituted vinylcyclopentanes [742]. The configuration of the double bond plays an important role in the cyclization in 9-(tributylstannyl)-7-octenals. Thermal activation of the (*Z*)- and the (*E*)-isomers leads to the same *cis*-vinylcyclohexanol, while under Lewis acid activation the (*Z*)-isomer gives the *cis* and the (*E*)-isomer the *trans*-vinylcyclohexanol [743]. The presence of an oxygen [744–746] or a nitrogen in the chain leads [747] to the same selectivity. This cyclization has been used in the preparation of a seven-membered oxygenated heterocycle in a synthesis of hemibrevetoxin B [748]. The intramolecular 1,2-addition of a chiral α -alkoxyallyltin group to an α,β -unsaturated aldehyde allows the formation of a 14-membered ring in the key step of an efficient synthesis of a (+)-cembranolide V [749].

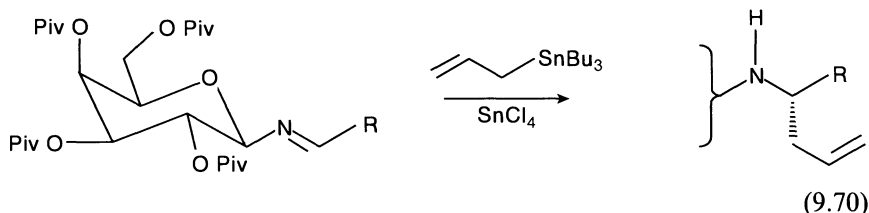
Substitution reactions. Allyltin compounds are not only capable of nucleophilic addition to the carbonyl of aldehydes, they can also be involved in nucleophilic substitution with reasonably activated partners such as acetals or acid chlorides. Again, stereoselectivity is one of the main features of these reactions. Under titanium chloride assistance, *cis*-2,5-disubstituted-1,3-dioxanes yield one of the opened isomeric allylated compounds while the *trans*-dioxane gives the other one. An oxocarbenium ion intermediate is shown to be involved in this reaction [750, 751].





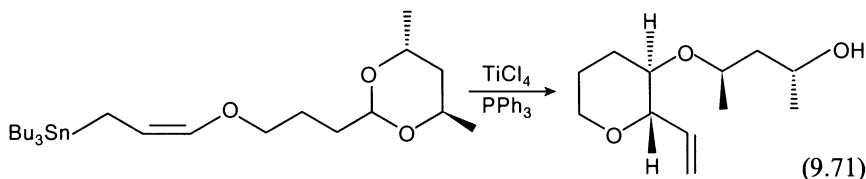
Allylation of an acetal stereoselectively substituted on the aldehyde moiety in the 3- or 4-position takes place with a very high remote asymmetric induction [752]. The same stereoselectivity is recorded in sugar chemistry [753]. Epichlorohydrin is not substituted at the activated chlorine but undergoes ring opening with allyltins to give 1-chloro-5-alken-2-ols. No elimination of the alkoxytin intermediate is reported [754]. The chlorine atom of acyl chlorides is reactive enough to couple with allyltins in the presence of an ammonium catalyst as an additive. This reaction is a good entry to allyl ketones [755]. Selenoacetals are also monosubstituted by allyltins [756] and *N*-acyl-*N,O*-acetals undergo displacement at the alkoxy group [757]. Chlorine, oxygen and selenium are not the only elements to be substituted by allyltins. Hydrogen can also be substituted, under palladium catalysis, when methylene groups are substituted by electron-withdrawing groups [758]. γ -Epoxyallyltins cyclize to give the greater cycle selectively under titanium catalysis. With an oxygen in the chain, functionalized oxepanes are obtained [759]. However, the substituents on the epoxide moiety play an important role in the regioselectivity of the cyclization [373]: both five- and seven-membered rings are accessible by intramolecular ring-opening of epoxides by allyltins, depending on the nature of the substituents, hydrogen or alkyl groups.

With optically active acetals derived from D-mannose, very high enantioselectivity is achieved, far better with allyltins than with the corresponding silicon or germanium reagents [760, 761].



Additions to nitrogen derivatives. Addition reactions of allyltins are not limited to aldehydes and ketones. They also react with aldimines under Lewis acid activation to give preferentially *syn* adducts with γ -substituted allyltins [762]. Acyliminium ions behave in the same way, when applied in a synthesis of statine [763]. Mild trimethylchlorosilane is found to catalyze the condensation [764]. Asymmetric synthesis of homoallylamines can be achieved either

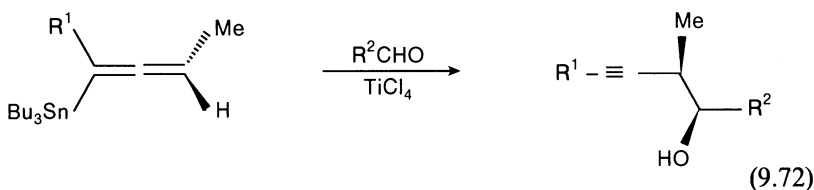
by using a chiral glycosyl [765] or a chiral phenylethyl [766] group on the nitrogen. Under transmetallation conditions alkoxyallyltins add to *N*-alkoxycarbonylimines with high asymmetric induction [767]. When imines are substituted by a chiral group, the stereochemistry is controlled by the configuration of the tin compound [768].



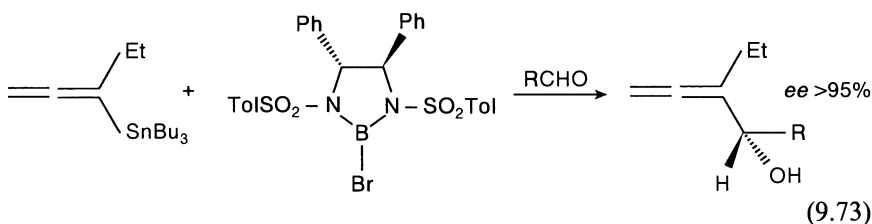
An allyl group can be introduced on nitrogen heterocycles by a 1,2-addition of allyltins, usually promoted by the use of an acyl chloride as activating agent. Pyridines [769, 770], isoquinolines [771], azoles [772] and imidazoles [773] undergo such an addition. It has been used in the synthesis of nirurin [770], berban and yohimban [771]. Addition of pentadienyltins with an unsaturated acyl chloride is followed by an internal cycloaddition leading to bicyclic compounds [774]. In the presence of $\text{BF}_3\text{-Et}_2\text{O}$, allyltins add to nitrile oxide to give oximes [775].

Propargyl- and allenylorganotin. Despite the easy 1,3-isomerization of propargyltins into allenyltins and vice versa, under Lewis acid activation, the ambident behavior of these reagents is easy to control and both allenyl- and propargyltins undergo clean additions to carbonyl compounds: allenyltins give homopropargylic alcohols while propargyltins lead to 2,3-butanediyl alcohols. Most of the recent applications of these compounds deal with enantioselective synthesis.

Allenyltins add in a 1,4-fashion to α,β -unsaturated carbonyl compounds and α -nitro olefins to give the corresponding propargylation products when the reaction is conducted in the presence of titanium tetrachloride [776]. With a chiral titanium alkoxide, addition to aldehydes gives homopropargyl alcohols with very high enantiomeric excess (>95%) [777]. Chiral homopropargyl alcohols can also be reached by adding chiral allenyltins to aldehydes. Simple aldehydes give *syn* alcohols while chiral α -substituted ones lead to *syn-syn* or *syn-anti* adducts depending on the configuration of the allenyltin and the nature of the Lewis acid [778].



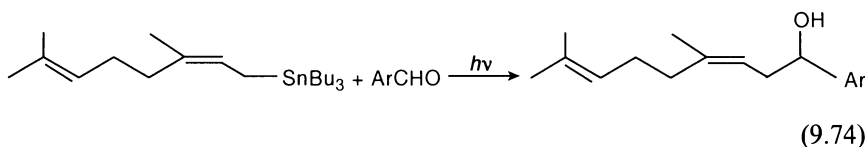
As allyltins, propargyl- and allenyltins can be transmetallated with tin tetrachloride before addition to carbonylated compounds. *Anti* additions are reported. So, by varying the nature of the Lewis acid and the order of addition of reagents, which can imply transmetallation, it is possible to obtain *syn-syn*, *syn-anti*, *anti-syn* or *anti-anti* adducts [779]. The use of trichlorobutyltin as catalyst instead of tin tetrachloride changes the chemoselectivity of the reaction: 2,3-butadienyl alcohols are then formed [780] from allenyltins. Chiral transmetallating agents such as boron derivatives are also very efficient and give high enantiomeric excess of buta-1,2-dienols or but-3-ynols from propargyl- or allenyltins and aldehydes [781].



Like allyltins [697], allenyltins add to silyl enol ethers. Reaction of 3-(phenylthio)allenyltins to silyl enol ethers proceeds with transposition to give the coupling products, 3-alkynyl-2-(phenylthio)ketones with complete stereoselectivity [782]. Substitution of acetoxy group is also possible under silicon triflate catalysis. Thus 4-acetoxy-azetidinones are propargylated by allenyltributyltin to give 4-(2-propynyl)azetidinones [783] in a more efficient way than by the corresponding Grignard reagent. Allenyltins react with cyanoacetates under palladium catalysis to give 2,5-dicyano-3-methylenehexanedioic acetates resulting from addition-substitutions [784].

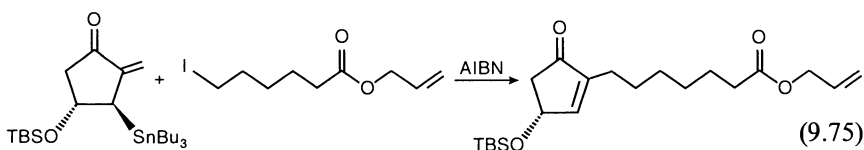
Radical and photochemical reactions. The weakness of the tin-allyl bond allows it to undergo not only electrophilic or nucleophilic cleavage but also homolytic cleavage. The reaction proceeds through addition, in mild conditions, of the carbon radical to the double bond of the allyltin or to the triple bond of propargyltins [785]. It is not especially fast, 10^4 – $10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 60°C , only about ten times faster than the addition to simple alkenes, and is followed by the rapid elimination of a tin radical [786]. It is most often used with halides, sulfides or selenides and benefits from all the advantages of radical reactions, mild conditions and tolerance to a large number of functionalities. It is also efficient with allyltrihalogenotins [787].

This selectivity is shown in the allylation of cyclic sugars, lyxopyranose and C-glycoside, in either 1- or 5-positions from the corresponding chlorides [788] or bromides [789]. The α -side chain of prostaglandins can be grafted onto the five-membered ring from a 2-methylenecyclopentanone, 3-substituted on the ring by a tributylstannyl group, with total allylic transposition [790].



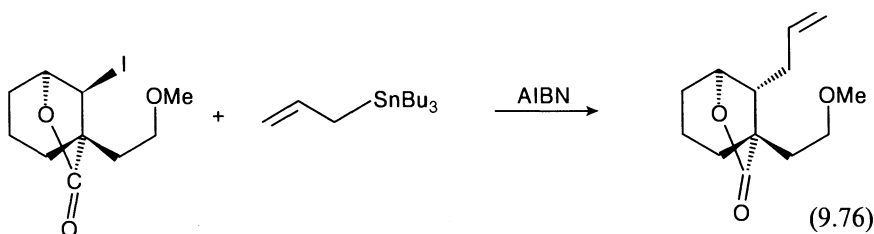
When a trimethylsilyl group substitutes the allyltin in the 2-position, coupling also occurs, even in the presence of an unprotected organic acid. Further oxidation of the silyl-vinyl bond to a carbonyl group makes this silylated allyltin a useful equivalent of an acetyl group introduced under neutral conditions [791]. An electron-attracting group in the same position, as cyano [792] or ester [793] does not interfere with the coupling with halides. Pentadienyltins give linear products with bridgehead halides [794].

Stereoisomers can be formed when substituted halides are used. With substituted acyclic halides diastereoisomeric excess can be very high [795], regardless of the composition of the starting material [796]. When it is possible, as with a β -methoxy- α -haloester, chelation with a Lewis acid increases the diastereoselectivity to a very high level [797, 798]. The conformation of the radical intermediate was shown with α -sulfinyl halides to be the major factor affecting the stereoselectivity [799, 800]. When cyclic halides are used, the reaction is also very selective [801]. Allylation of bromopenems takes place with inversion of the configuration [802].



Monoallylation of cycloalkanones can be easily achieved through the coupling of 2-(phenylseleno)cycloalkanones with allyltins under radical conditions. Substituted ketones lead preferentially to *trans* adducts [803], as do oxazolidin-2-ones [804]. The same selectivity is recorded in the allylation of substituted 2-(phenylseleno)lactones [805] and 4-(phenylthio)lactones [806]. Allyltins can be involved in three-component radical reactions where the radical adding to the allyltin is not created from a halide but generated by addition of a radical to an alkene. The combination of a phenylthioether, an α,β -unsaturated ketone and an allyltin gives 3-alkyl-2-allylketones in good yields [807]. Vinyltins can be used as well [808].

Allyltins are good candidates as electron donors in photoinduced single electron transfer processes since their cation radicals undergo easy fragmentation to give allyl radicals and trialkyltin cations. These allyl radicals add to aldehydes or ketones, stereospecifically when they are substituted, to give linear adducts [809]. The same selectivity occurs with acridinium ions, while thermal reaction results in the linear isomers [810].

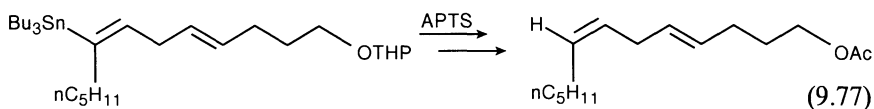


With unsymmetrical α -diketones, the allyl group adds to benzoyl carbon, which is the reverse of what is observed in the presence of boron trifluoride, where allylation occurs on the acyl carbon [811]. The epoxy group of α -epoxyketones is opened by addition on the central carbon [812] to give 2-allyl-3-hydroxyl ketones while substitution occurs with cyanobenzenes [813].

9.2.4 Electrophilic cleavage of tin-carbon bonds

The sensitivity of organotin reagents to cleavage by common electrophilic reagents such as acids and halogens makes these organometallic compounds very useful for the introduction of hydrogen, deuterium or halogens in a molecule. Furthermore, this reaction can be extended to nitrogen, sulfur and selenium, which gives an interesting entry to amines, sulfides, sulfoxides or sulfones, and selenium compounds. Again, these reactions are characterized by their very high selectivity which allows them to be used with compounds bearing a wide array of functional groups. The synthesis of radiopharmaceuticals via electrophilic demetallation of organotins has been reviewed [814].

Access to carbon-hydrogen and carbon-deuterium bonds. Synthesis of deuterium-labeled natural sesquiterpenes isoalantolactone and alantolactone is achieved by reaction of the corresponding (tributylstannyl)lactone with trifluoroacetic anhydride in the presence of deuterium oxide. The cleavage of these vinyltins leads to 6:1 mixtures of isomers and corresponds to a retention of configuration at carbon, with a better selectivity than the deuteration in the same position by reduction of a vinylsulfoxide by NaBD_4 [90]. *p*-Toluenesulfonic [815] and acetic [816, 817] acids in methanol lead to stereospecific cleavage of vinyltins in a synthesis of insect pheromone [815] by cleavage of a tin-vinyl bond and in the deuteration of bicyclic thioethers [816].

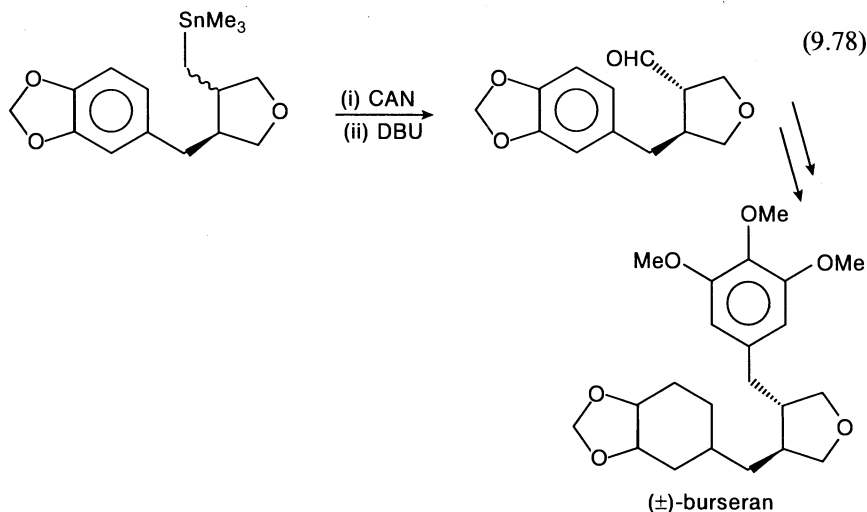


Hydrolysis of methyl (stannyl)crotonates with hydrochloric acid in

methanol reveals considerable differences in rates depending on the position of the tin on the double bond, smaller values being recorded with β -stannyl esters [818]. When activated by a geminal fluorine atom, vinyltins are susceptible to cleavage in a neutral medium, with cesium fluoride in methanol, or in a basic medium, with sodium methanolate. Both conditions have been used in a synthesis of acid-sensitive (fluorovinyl)nucleotides [819].

Access to carbon–nitrogen bonds. Organotin compounds can be transformed in various nitrogen derivatives such as nitroso or nitro derivatives. They can also be useful starting materials for the preparation of diazenes when they react with benzenediazonium tetrafluoroborates [820].

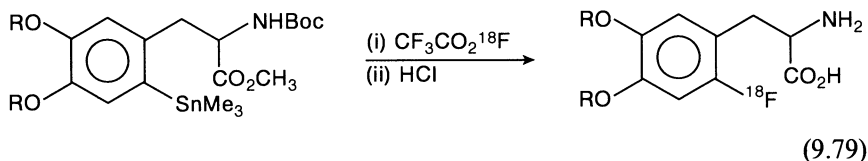
Access to carbon–oxygen bonds. Classical transformations of carbon–tin bonds to carbon–oxygen bonds with lead tetraacetate are still exemplified. However, new processes involving singlet oxygen or electron-transfer reaction have recently emerged. Alkyl carbon–tin bonds can be cleaved by 3-chloroperoxybenzoic acid to give alcohols in good yield with retention of configuration at carbon [821–823]. The reaction can be conducted in the presence of free hydroxyl groups [824]. While benzyl- and α -heteroalkyltins are oxidized to the corresponding esters even in the presence of a free hydroxyl group at positions 4, 5 or 6, the course of the reaction is different with hydroxyl groups at positions 3 and 5. In this case an oxidative cyclization takes place, leading to 3-hydroxytetrahydropyran [825]. It is also possible, with ozone, to obtain carbon–oxygen double bonds. α -Alkoxyalkyltins are then transformed into esters [826]. The same transformation [827], or a related one leading to acetals [828] can be conducted with ceric ammonium nitrate. It has been used in a synthesis of (+)-burseran [827].



The oxidation of benzyl- or α -heteroalkyltins either electrochemically [829], with copper tetrafluoroborate under irradiation [830] or with ceric ammonium nitrate [831] leads to ethers when alcohols are used as nucleophiles. When heated with chromium oxide, 2-alkoxyalkyl-2-cyclopentyltins give the corresponding unrearranged ketones while, with 3-chloroperbenzoic acid, the corresponding transposed alcohols are obtained [832] from terpenyltins. Lead tetraacetate gives the corresponding acetates without transposition [833]. Oxidation of 2-furyltins with the same reagent does not give the expected ester. It leads to the product of further oxidation, 5-acetoxymethyl-2(5H)-furanones. The synthetic utility of this transformation is exemplified in a short synthesis of tricyclic anemonin [834]. Reaction of tetraallyltins with singlet oxygen gives tetraallylperoxytins which can further react with aldehydes to give 1,2,4-trioxanes [835].

Access to carbon-halogen bonds

Fluorides. Two new reagents for the fluorination of double bonds via vinyltins, xenon difluoride and cesium fluoroxysulfate, are shown to be also convenient with aryltins. In the presence of catalytic silver salts, which could indicate some transmetallation process, vinyltins are cleaved by xenon difluoride in very mild conditions to give selectively the corresponding fluorides [836]. This reaction has been applied to a synthesis of fluorine analogs of cannabinoids [837]. Cesium fluoroxysulfate is also a mild and selective source of electrophilic fluorine to transform vinyltins into vinylfluorides with a reasonable yield, providing that methanol is used as a cosolvent [838]. Both 2- and 3-fluoroindoles, or 4-fluorosteroids are obtained from the corresponding stannylindoles [839] or stannylsteroids [840]. Fluorodestannylation of aryltins can be carried out with elemental fluoride in good conditions. This process is applied in the synthesis of fluorinated tyrosine [841] and dopamine [842] derivatives, and of imaging tracers [843]. In the case of dopa, acetyl hypofluorite can be used as well [844].

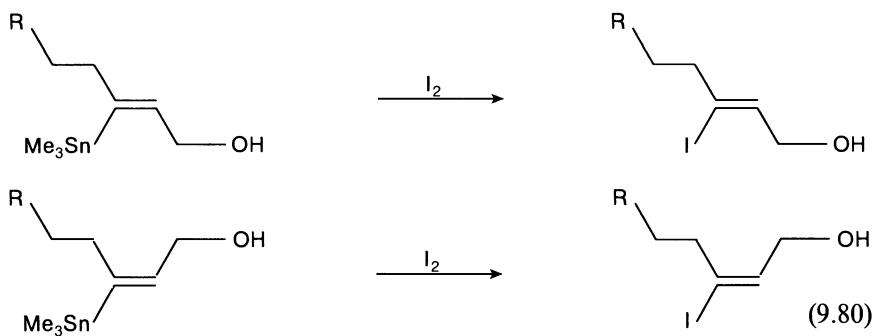


It is worth mentioning a fluorodestannylation method by electrosynthesis. In this reaction, α -oxygenated- ω -unsaturated tins give fluorine containing heterocycles [845] after anodic oxidation in the presence of ammonium fluoroborate.

Bromides. Radiobromination of estrogens [846, 847] or benzodiazepines [848] is accomplished by treating vinyltins or aryltins with ammonium

bromide [846, 847] or sodium bromide [848] and chloramine T in an acidic medium.

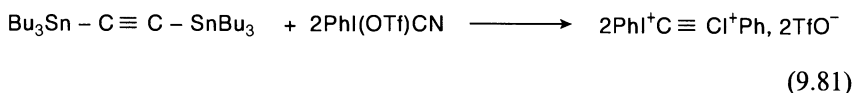
Iodides. In contrast to fluorides where the halogen is a dead-end unreactive function, iodides are often involved as intermediates in synthetic schemes. No major improvement in their preparation from organotins has been reported during the last decade and vinyl iodides have been the more important targets. The stereoselectivity of the cleavage, the retention of configuration at carbon, is usually total, greater than in the preparation of fluorides. The cleavage of 2-methyl-cyclopropylcarbinyln tin proceeds preferentially with ring cleavage and addition to the unsubstituted methylene to give a primary homoallylic iodide [849]. The presence of the carbonyl of a ketone does not interfere with the cleavage of a tin–vinyl bond by iodine, when it is α to the metal [850] or in a more remote position [851]. α - [852], γ - [853] or ω - [854] Stannyl esters are equally well transformed into the corresponding iodides. This process was applied in syntheses of allylglycine derivatives [853] and avermectins [854]. Alcohols substituted in various positions by an iodovinyl group are easily reached from the corresponding stannylvinyl alcohols and iodine. Iodoallylic alcohols with either internal [855] or external [856–859] iodine atoms are prepared in this way and used in syntheses of (+)-alloprimilotoxins [855], leukotriene B4 [856], stereodefined iodocyclopropanes [857] and ^{125}I -labeled nortestosterone derivatives [858].



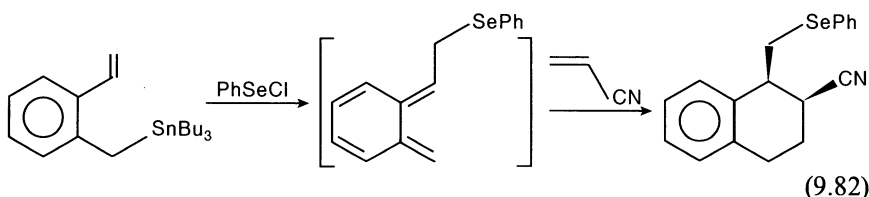
This access to iodoalcohols is also effective in the case of iodohomoallylic alcohols [859] and ^{125}I -labeled diprenorphine [860]. Applications in various synthetic schemes include preparations of diterpenoids (+)-kolavenol and (–)-agelasine B [861], erythronolide templates [862] and 2-iodocyclohexenone acetal [179]. When two vinylic tins are present in the same molecule, they can be either simultaneously or successively cleaved with iodine [863].

Aryltins show the same reactivity as vinyltins towards iodine. They are selectively transformed into the corresponding iodides even in the presence of various functional groups such as esters [864], amides [864], amines [865],

alcohols [866] or diazirines [866]. When a trimethylstannyl group is *ortho* substituted by a nitro group, methyl-tin bond cleavage becomes preponderant [867]. Iodonium salts can also be reached through organotin compounds. Thus aryl and heterocyclic tins react with (dicyano)iodonium triflate to give the corresponding diorganoiodonium salts and tributyltin cyanide as by-product [868]. Phenylcyanoiodonium triflate also reacts with alkynyltins to give the corresponding alkynyl(phenyl)iodonium triflate, even in the presence of a carbonyl or cyano group [869]. Distannylacetylene leads to the bis(iodonium) species [870].



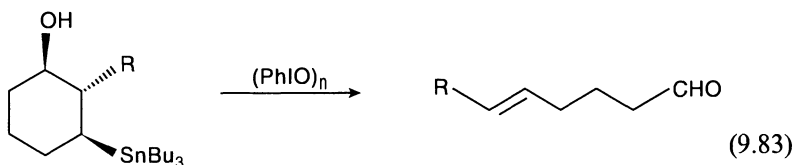
Access to sulfur- and selenium-carbon bonds. Organotins, especially trifluoromethyl, aryl and vinyltins are very good precursors of sulfur and selenium derivatives. When they are opposed to arenesulfonyl halides [871, 872], trimethylsilyl chlorosulfonate [873] or sulfonyl chloride and secondary amines [874], they lead to sulfones, sulfonates or sulfonamides, respectively. The combination of the electrophilic cleavage of tin-benzyl bonds in (*ortho*-alkenylbenzyl)tins by sulfenyl or selenyl chlorides and the cycloaddition of the resulting *ortho*-quinodimethane gives bicyclic thio or seleno ethers in good yields [875, 876].



Substituted 5-pentenyltins undergo an addition-elimination process with *N*-phenylselenophthalimide which leads to (phenylselenylmethyl)cyclopentanes. Such cyclization is specific to the 5-hexenyl group; 6-heptenyl or 4-heptenyl groups do not give cyclization compounds [877].

Access to carbon-carbonyl bonds. When activated by an α -heteroatom, carbon-tin bonds do not require the presence of a transition metal catalyst in order to be cleaved by acyl chlorides. 1-Sulfonylvinyltins and 1-sulfonylcyclopropyltins react with acyl chlorides in refluxing toluene to give the corresponding ketone in good yields [878]. This reaction does not follow the same course with the corresponding sulfoxides. A Pummerer-type rearrangement occurs leading to the corresponding sulfide-enol esters [879]. With titanium tetrachloride as coreactant, vinyltins bearing a geminal substituent at the 1-position react with acyl chlorides at the terminal position. *Ips*o substitution

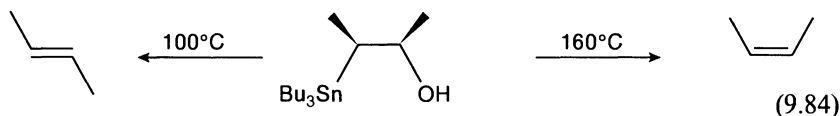
is completely inhibited, probably for steric reasons [880]. In the same conditions, with a trimethylsilylmethyl group as geminal substituent, the non-*ipso* reaction is accompanied by a 1,2-silyl shift which results in the isolation of 2-trimethylsilyl-2-propenyl ketones [881]. Tin-carbon bond cleavage by iodosylbenzene can be followed in cyclic γ -stannyl alcohols by a Grob fragmentation leading to ω -unsaturated ketones [882].



9.2.5 Elimination reactions of organotins

The presence of a heteroatom at the β -, γ -, δ - or ω -position weakens the tin-carbon bond strength and allows 1,2-, 1,3-, 1,4- or 1,*n*-elimination to occur, giving either unsaturated or cyclic organic compounds.

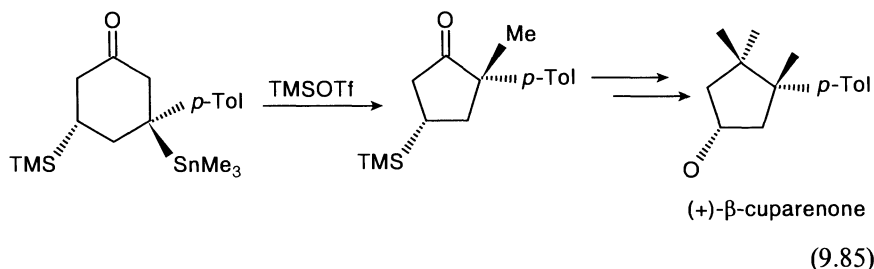
1,2-Eliminations. Allylic zirconium compounds with a tin at the γ -position, prepared by hydrozirconation of 1,2-propadienyln, add to aldehydes with transposition to give α -stannylallyl alcohols which undergo a 1,2-elimination. (*E*)-1,3-dienes are finally obtained [883]. 1,2-Elimination is also efficient with β -stannylated allyl alcohols when the alcohol is transformed in mesylate, leading to allenes [884]. β -Epoxy- β -stannyl alcohols undergo the same reaction, when transformed in mesylates, to give methylene-oxiranes [885]. Conjugate addition of stannyl lithium to α,β -unsaturated α -phenylselenocyclanones leads, after alkylation of the resulting enolates by aldehydes, to β -selenostannyl intermediates which undergo spontaneous elimination providing an efficient synthetic method for α -hydroxyalkylcycloalkenones [886]. When allyl halides are used as trapping agents, this reaction provides an efficient route to chiral prostaglandin E_2 key intermediate [887]. The stereochemistry of this type of reaction has been studied. Thermal elimination in (β -acetoxyalkyl)tins or (β -hydroxyalkyl)tins are *anti* eliminations [888]. However, in the case of (β -hydroxyalkyl)tins a reversal of selectivity leading to *syn* elimination is observed at higher temperatures [889].



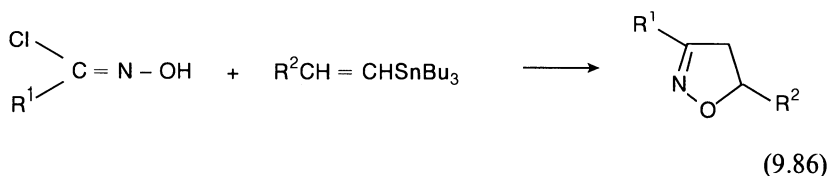
There are very high stereochemical requirements for this reaction to occur. When an *anti* arrangement cannot be reached, the elimination does not occur

[890]. When it is performed under basic conditions, the postulated four-membered intermediate 1,2-oxa-stannetanide has been characterized as a potassium salt [891]. Eliminations of organotin compounds can also occur via carbanions. Thus under reaction with a strong base, β -stannyl nitriles undergo a clean 1,2-elimination giving the corresponding acrylonitriles [892].

1,n-Eliminations. 1,3-Eliminations are also interesting synthetic tools. Under the influence of a Lewis acid [893] or when the hydroxyl is transformed into a better leaving group [894] γ -stannyl alcohols achieve the construction of cyclopropane rings according to a stereospecific process. The same reaction occurs with (3,4-epoxybutyl)tins. Stereochemical requirements are very high in order to obtain good results. In spirocyclic compounds, a w-arrangement of the atoms involved in the 1,3-elimination, which involves inversion at both carbon centers, is necessary. It led to a precursor of hirsutene [895]. In the presence of Lewis acids, β -stannyl cyclanones, prepared from cyclanones, are sufficiently activated to undergo a 1,3-elimination giving unstable bicyclic cyclopropanols which open up to give cyclanones, the ring being one atom short [896]. It has been applied to a synthesis of (+)- β -cuparenone [897].



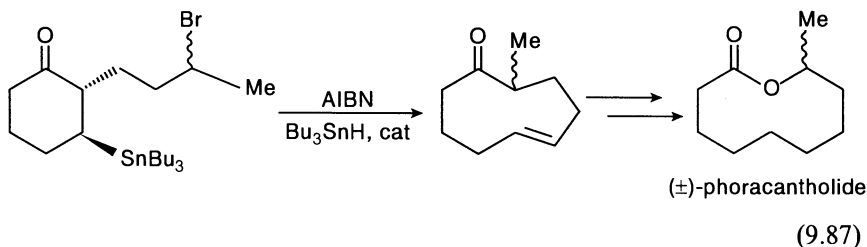
Another type of elimination occurs with β -stannyl ketones. When treated with 3-chloroperoxybenzoic acid they undergo an oxidative fragmentation with a very high regioselectivity giving acids where both carbons between the carbonyl and the tin are removed. Tin was found to be superior to silicon in this reaction [898]. Starting from α -ethylidene cycloalkanone, addition of stannyl lithium, alkylation with an electrophile and treatment with a Lewis acid leads by the same reaction to β -allylidene cycloalkanones having an extra member [899]. Treatment of chiral substituted (4-hexene-2-yl)tin by iodine in the presence of silver triflate results in a selective 1,5-hydrogen shift leading to substituted 6-iodo-1-hexene with a very high level of chirality transfer [900]. Access to cyclopentanol or cyclohexanol is allowed by the carbocyclization of δ - or ϵ -stannyl ketones under the influence of Lewis acids. It is specific to these types of cycle [901]. When they react with hydroximoyl chlorides, vinyltins have two roles: first, they act as a base to generate nitrile oxides and second, they provide an unsaturated moiety capable of undergoing a [3+2] cycloaddition leading to isoxazolines [902].



α -Heterocarboanion intermediates can be generated from the corresponding α -heteroallyltins by oxidation, either anodic or with ceric ammonium nitrate. Thus alkoxymethyl, aminomethyl, thiomethyl [903], 1,3-dithianyl [904] or (methoxycarbonyl)methyl [905] groups can be introduced on suitable partners such as electron-rich olefins. It also allows an interesting preparation of isonitriles and nitriles with trimethylsilyl cyanide [906]. An analogous reaction is that of 1-(phenylthio)vinyltins and arenes when they are treated with tin tetrachloride. Transmetalation to trichlorovinyltins occurs, which are capable of nucleophilic attack on various arenes to give substituted [1-(phenylthio)vinyl]arenes [907].

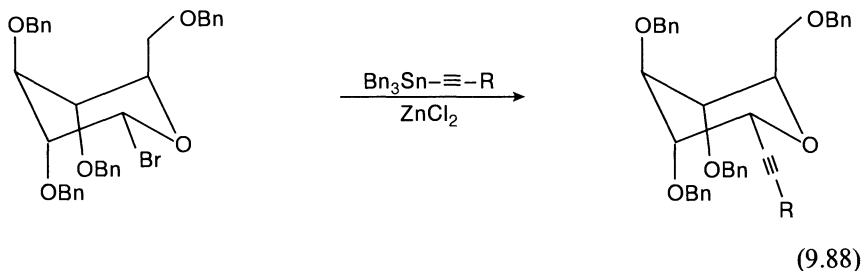
9.2.6 Reactions of miscellaneous organotins

Radical reactions of vinyltins. 1-Alkenyl groups can be grafted on organic compounds through radical coupling reactions. Treatment of 1-alkenyltins with iodides under radical conditions leads to the coupled compounds without loss of stereochemistry of the starting organotin [908]. It was used in sugar [909] and heterocyclic chemistry [910]. Radical conditions can lead to eliminations with skeleton rearrangement. Various cyclanones, α -substituted by an ω -halo chain and β -substituted by a tin, undergo halogen abstraction with tributyltin hydride followed by a rearrangement leading to large-ring cyclanones [286].



Reactions of alkynyltins. Alkynyltins add to carbonyl compounds in the presence of Lewis acid. Trichloroalkynyltins, prepared *in situ* from alkyne and tin tetrachloride in the presence of a tertiary amine, also do so. They monosubstitute acetals and add in a 1,4-fashion to α,β -unsaturated ketones [911]. Coupling with activated halides, such as α -alkoxyhalides in α -D-glucopyranosyl bromide [912] or allylic halides [913], is successfully achieved

with silver tetrafluoroborate or nickel complexes as catalysts, respectively. With D-ribofuranosyl bromide, the α -substitution is preferably obtained [914].

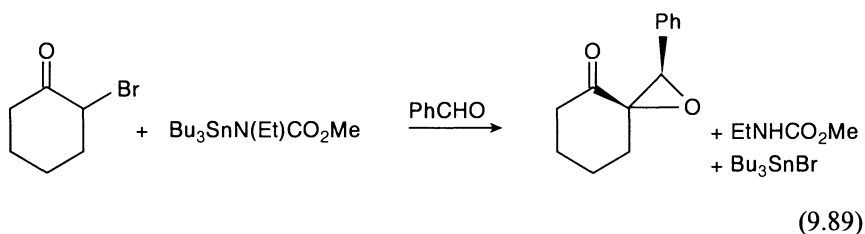


In the presence of Lewis acids, acetals react similarly. The reaction, which is a clean inversion at acetalic carbon [915] can give either enantiomer with chiral acetals, depending on the nature of the inducing moiety [916]. 2-Ethoxypyrrolines, which are *N,O*-acetals, are alkynylated at position 2 by alkynyltins in the presence of tin triflate [917]. Alkynyltins add to pyridine [918] and related compounds [919] in the 2-position in the presence of chloroformates as activating agents. With 3-acylpyridines, the alkynyl group is preferentially introduced at the more hindered position to give 2,3-disubstituted 1,2-dihydropyridines [918]. α - or β -Enones can be obtained selectively when ketones are treated with trichloroalkynyltins, generated *in situ* as mentioned above, the internal alkynyl carbon being linked α to carbonyl [920]. Silyl enol ethers lead to α -enones [921], and the same reaction allows *ortho*-alkenylation of phenols [922]. With nickel salts as catalysts, a three-component reaction occurs between enones, 1-alkynes and alkynyltins. It leads to stereo-defined (*Z*)-3-en-5-ynones with the hydrogen from the 1-alkyne at the 3-position [923].

9.3 Applications of tin-heteroatom bonded compounds

9.3.1 Reactions of organotins with nitrogen-tin bonds

Palladium-catalyzed aromatic amidation of aryl bromides with tin amides is successful with either preformed tin amides [924] or *in situ*-generated reagents [925] by transamination from dimethylaminotributyltin. Tin(II)amides are very effective for the conversion of esters [926] or acids [927]. The reaction takes place under very mild conditions and tolerates carbonyls of ketones and hydroxyl groups [926]. A stannylcarbamate, obtained by addition of methoxytin to ethyl isocyanate, is able to promote a novel Darzens-type reaction under mild and neutral conditions. Thus, treatment of α -halo ketones with aldehydes leads to epoxy ketones even with α -halo ketones bearing enolizable α' -hydrogens [928].



The same tin reagent leads to a Michael addition with α -halo ketones and α,β -unsaturated ketones. Diacylcyclopropanes are obtained with a very high *anti* selectivity [929].

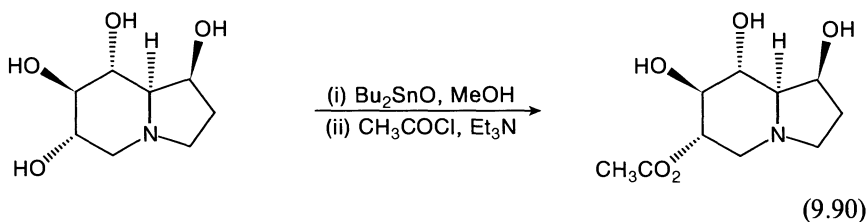
Tin azides convert nitriles and amides into tetrazoles [930]. These heterocycles are also obtained from nitriles without tin azides by using silyl azides in the presence of dibutyltin oxide as catalyst [931]. Tin azides act as nucleophiles with oxiranes which are opened from the less hindered side to give 1,2-azido alcohols [932].

9.3.2 Reactions of organotins with oxygen-tin bonds

Organotin alkoxides

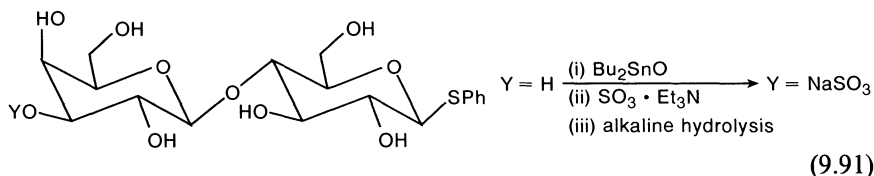
In substitution reactions. The stannylation of the hydroxyl group is a good way to increase its nucleophilicity. Thus, monohydroxylated compounds can be activated as tributylstannyl ethers while polyhydroxylated compounds can react as polytributylstannyl ethers but more usually, after reaction with Bu_2SnO , as dibutylstannylene acetal derivatives. It is interesting to note that the stannylene acetal formation is efficiently accelerated by microwave heating [933] and that even catalytic amounts of Bu_2SnO can be sufficient to achieve high levels of substitution [934]. An important technical improvement has been the preparation of stannylene acetals from diols (or polyols) and $\text{Bu}_2\text{Sn}(\text{OMe})_2$ in benzene, a method which affords simplicity, improved solubility and reproducibility [935]. It is now clear that the results, in terms of regioselectivity, are linked to the auto-association of the stannylene acetals which behave as dynamic mixtures of oligomeric species, although they are usually dimeric [936].

Acylation of hydroxyl groups of non-carbohydrate derivatives. The selective monoesterification of diols by reaction of dibutylstannylene acetals with acyl chlorides has been rationalized [937] and applied to simple cases, such as the monoacylation of 2,2'-binaphthol [938]. Most illustrative are the cases of regioselective monoacylation of unsymmetrical diols [939, 940] which can occur at the usually more reactive site (primary alcohol) [941] but also, interestingly, at the most substituted site [942]. A spectacular case of monoacylation of castanospermine is worth mentioning [943]:



Numerous preparations of macrocyclic lactones have been reported by the reaction of dibutystannylene acetals with cyclic anhydrides [944] or diacyl dichlorides [945, 946]. In most cases the dimeric stannylene acetals lead to mixtures in which dimeric tetralactones are obtained in good yields [947], while a debate is still open as to whether the tin atoms exert a template effect [948] or if the composition of the oligomeric mixture of polylactones is under thermodynamic control [947]. Diols protected as tributylstannyl ethers can be similarly employed [945].

Acylation of hydroxyl groups of carbohydrate derivatives. The regioselective manipulation of hydroxyl groups in carbohydrates, via organotin intermediates, is now a routine technique which cannot be exhaustively reviewed here. Some examples can be cited for glucose derivatives [949], D-xylopyranosides [950], thymine nucleosides [951], glycals [952] and cyclodextrins [953]. Sulfation of glycosides has been performed by this method [954] with spectacular examples leading to selective reactions without protection of other hydroxyl groups [955]:

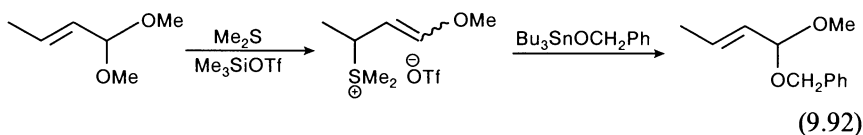


An efficient synthesis of *myo*-inositol derivatives has been presented which involves initial borylation, transmetallation with $\text{Bu}_2\text{Sn}(\text{acac})_2$ and acylation with menthyl chloroformate [956].

It appears that the reasons for a regioselective substitution at a specific site are complex. Equilibrating intermediates are involved in some cases [957, 958] and differences between neighboring groups in others [959]. It is interesting to note that the nature of the group bound to tin is important. Thus hexamethylene stannylene acetals are tosylated at a secondary hydroxyl group while the dibutylstannylene equivalents react in preference at a primary hydroxyl group [960]. Again, the explanation involves equilibrating dimeric species [961].

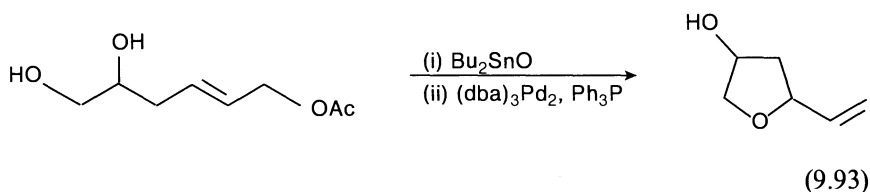
Alkylation of hydroxyl groups. Selective monoalkylation of acyclic diols with Bu_2SnO , in the presence of fluoride ions, occurs at a primary hydroxyl group [962] and kinetically controlled regiospecific reactions of polyols have been performed, with striking differences when the electrophile is a silylating agent [963]. Again, most applications deal with carbohydrates. Amongst numerous data, it is possible to select the regioselective silylation of ribonucleosides using Bu_2SnO , which never occurs at the 2'- and 3'-position, even with excess reagent [964], and the regioselectivity of tributylstannyloxy-mediated benzylations, in the presence of *N*-methylimidazole, which modifies the equilibrium position of the stannylated species [965]. Dibutylstannylene acetals of *myo*-inositol have been selectively allylated, as a function of the quantity of Bu_2SnO employed [966], while borylated *myo*-inositol was exchanged with the tributylstannyl enolate of pentane-2,4-dione to give very regioselective *O*-alkylation [967]. Several very recent examples illustrate well the efficiency of the method, especially for the preparation of oligosaccharides from unprotected substrates [968–971].

Miscellaneous substitutions. Vinylic fluorine atoms can be exchanged by alkoxy groups provided by tin alkoxides [972] which are also able to transform dinucleotide *S*-aryl phosphorothioates into the corresponding *O*-alkyl phosphates [973]. Also, *O*-stannyl ethers are accepted in lipase-catalyzed transesterifications in organic solvents [974]. Mixed α,β -unsaturated acetals have been obtained by substitution via alkenylene sulfonium salts [975]:



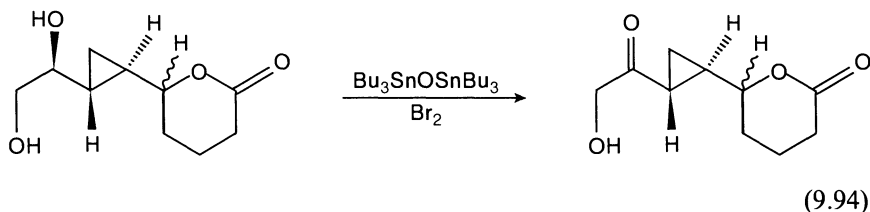
While tributylstannyl ethers of phenols can be glycosylated, in the presence of SnCl_4 , at the anomeric position of *O*-acetyl pyranosides [976], anomeric deacetylation of sugars usually occurs by reaction with tin alkoxides. The intermediate stannylated sugar is destannylated by an alcoholic solvent or isolated and reacted in an aprotic solvent [977]. However, an attempted debenzoylation with $\text{Bu}_3\text{SnOMe}/\text{LiCl}$, in the taxane series, was accompanied by opening of the oxetane ring [978]. The exchange of dibutylstannylene acetal with acrolein diacetate, in the presence of Pd catalyst, constitutes a new method for the protection of two OH groups in carbohydrates [979]. Also, the treatment of tin alkoxides with thiol acetates, in the presence of fluoride ions, gives thiostannanes which are efficiently reduced to disulfides by FeCl_3 [980].

A route to cyclic ethers has been found by intramolecular reactions of tin alkoxides with allyl acetates [981]:



Finally, the stannylation of hydroxyl groups appears to be an efficient improvement in processes such as the so-called 'sulfoxide glycosidation method' [982].

Oxidation reactions. The oxidation of alcohols, by reaction of their tin alkoxide derivatives with halogens, has become a popular reaction, extended to the case of vicinal diols which are transformed into diketones [983]. Selective bromine oxidation of tributylstannyloxy derivatives is obtained from complex multifunctional substrates such as oligosaccharide fragments of calicheamicin [984] or cyclopropane containing eicosanoids [985]:



Iodine can be used as oxidizing agent [986] in addition to *N*-iodosuccinimide [987]. The oxidations can be also performed through dibutylstannylylene acetal intermediates. Examples of regioselective oxidation of disaccharides show the important role of the solvent and the base employed for scavenging the hydrogen halide thus formed [988]. An explanation for the regioselectivity observed has been given [961]. CuBr_2 , in the presence of LiBr , and *tert*-butyloxytributyltin, as HBr scavenger, have been successfully applied to the oxidation of primary alcohols through their tributylstannyloxy derivatives [989]. It is worth mentioning the curious high-yield direct oxidation of 2-silatranyl-2-bromoethanol to 2-silatranylacetaldehyde by triethyltin methoxide [990].

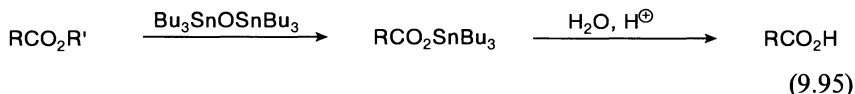
Addition reactions. Several spiro orthocarbonates have been obtained in high yield by reaction of dibutylstannylylene derivatives of diols with CS_2 [991], sometimes under the beneficial influence of added bases such as Bu_3P or Et_3N [992]. Tributylstannyloxy derivatives add to cumulenes such as isocyanates. This observation, coupled to the possibility of ring opening of γ -bromo- β -lactones with tributyltin methoxide, has opened a new route for the synthesis of heterocyclic compounds such as oxazolidinones [993]. Ring opening of

epoxides is facilitated when the hydroxyl group is activated by stannylation [994] and Pd-catalysis allows the ring opening of vinyl epoxides by tin alkoxides via intermediate tin *ate*-complexes [995]. Related to ring opening is the facile addition of tin alkoxides to intermediate three-membered complexes obtained by reaction of the carbon-carbon double bond of glucals with sulfonium [996] or iodonium salts [997]. New 2-deoxy- β -glycosides or deoxyfucosyl dissacharides are accordingly obtained.

As catalysts. Tributyltin methoxide (and also tributyltin oxide) catalyzes the lactonization of ω -hydroxytrifluoroethyl esters [998], while dibutylstannylene acetals of simple diols, either as dimers [999] or as complexes with Bu_2SnCl_2 [1000], catalyze the oligomerization of (*S*)- β -butyrolactone to macrocyclic polylactones. ϵ -Caprolactone can be also polymerized to polyesters by a variety of organotin catalysts, tributyltin methoxide being the most efficient [1001]. Similarly, a number of organotin compounds catalyze the reaction of carbon dioxide with methanol to give dimethyl carbonate, dibutyltin dialkoxides being particularly active [1002].

Other compounds

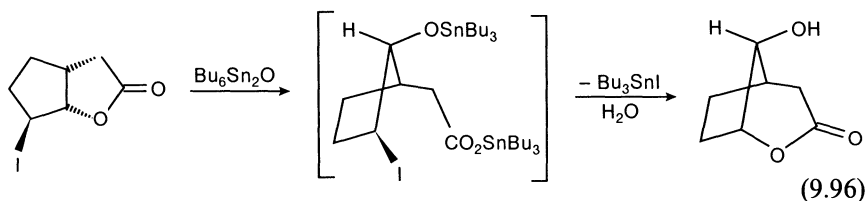
Triorganotin oxides (stannoxanes). A useful reaction of bis(tributyltin) oxide is its exchange reaction with esters which gives tributyltin carboxylates, easily hydrolyzed to carboxylic acids:



This mild method has found applications for the deprotection of various esters [1003], including sensitive penicellanate esters [1004]. Its scope and limitation have been described [1005]. Recently, the method has been applied to the non-hydrolytic deprotection of steroid acetates, with efficient recovery of the steroid hydroxyl part after flash chromatography on silica gel [1006].

In a similar way, phosphorothioate triesters, in nucleotidyl peptides or dinucleotides, undergo selective P-S bond cleavage with an excess of $\text{Bu}_6\text{Sn}_2\text{O}$ in neutral conditions [1007, 1008].

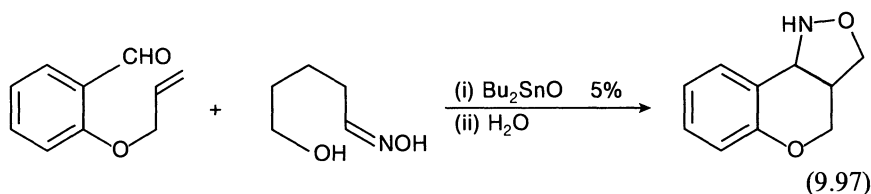
$\text{Bu}_6\text{Sn}_2\text{O}$ (as well as Bu_2SnO) can be employed for the conversion of thionocarbonates into carbonates or thionolactones into lactones by O-S exchange [1009]. On the other hand, *N*-tributylstannyl heterocycles have been obtained from $\text{Bu}_6\text{Sn}_2\text{O}$ and ω -haloalkyl isocyanates, with the possibility of further alkylation of the N-Sn bond [1010] and hydroxylactones have been prepared by $\text{Bu}_6\text{Sn}_2\text{O}$ -promoted ring expansion of halolactones [1011]:



Several catalytic uses of triorganotin oxides have been reported. Thus $\text{Bu}_6\text{Sn}_2\text{O}$, associated to molybdenum, catalyzes the epoxidation of alkenes [1012], while when associated to chromium it promotes the oxidation of various hydrocarbon substrates [1013, 1014]. Substituted distannoxanes, usually as dimeric double-layered species, play the role of templates and efficiently catalyze transesterification and esterification [1015], especially mono-transesterification of diol esters [1016], acetalization of carbonyls [1017] or carbamoylation of alcohols, with an interesting application to the determination of the enantiomeric excess of chiral alcohols [1018].

Triorganotin esters. The alkylation of tributyltin carboxylates in the presence of CsF yields esters, and the esterification can be realized with tin esters made *in situ* [1019], while tributylstannyl phosphates or *O*-alkyl phosphonates can be also alkylated [1020]. However, these compounds are mainly employed as catalysts or cocatalysts. Thus the triflate $\text{Bu}_2\text{Sn}(\text{OTf})_2$ catalyzes the acetalization of carbonyl compounds [1021], allows Michael additions and Robinson ring annulations with silyl enol ethers [1022], and is employed in glycosylation processes [1023, 1024]. Tributyltin acetate is a cocatalyst for Pd -catalyzed reactions involved in various syntheses of heterocyclic compounds [1025, 1026].

Miscellaneous. Dibutyltin oxide has been employed for the bromination of nucleosides, in neutral conditions, in the presence of alcohol nucleophiles [1027]. After pyrolysis with tributyl phosphate, it was shown to be an efficient mild catalyst for the deprotection of THP and silyl ethers [1028]. It is also used to catalyze the cyclization of amino acids to lactams [1029], the rearrangement of ketols [1030], but, more originally, allows a general procedure for the synthesis of *N*-substituted isoxazolidines via nitrone-olefin cycloaddition [1031]:



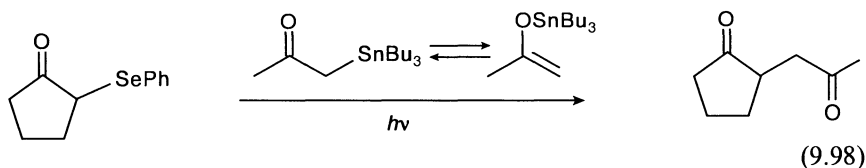
The oxidation of *O*-stannyl aldoximes (with BuOCl or NBS) [1032] or the reaction of hydroximoyl chloride with tributyltin oxide [1033] lead to intermediate nitrile oxides which enter into dipolar cycloadditions to give isoxazoles and isoxazoles in good yields.

Finally, tritylation, methoxymethylation and silylation of allylic hydroperoxides have been easily performed via stannyl peroxide intermediates (prepared by reacting tributyltin methoxide with the corresponding hydroperoxide) [1034] which can also undergo Fe(III)-induced cleavage to dicarbonyl compounds [1035]. In the presence of *tert*-butyl hydroperoxide, dibutyltin oxide gives dibutyltin oxyperoxide which is able selectively to epoxidize allylic alcohols [1036], while endoperoxides have been synthesized by reacting bis-triflates with hexabutylditin peroxide [1037].

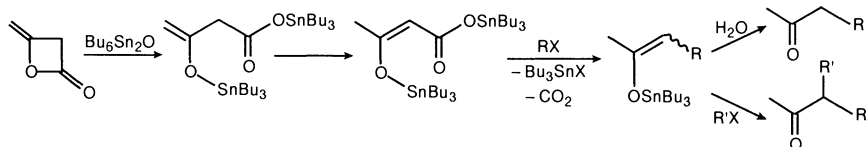
Organotin enolates

Tin(IV) enolates

In substitution reactions. Following Noyori's initial findings, organotin enolates (made by reacting triphenyltin chloride with lithium enolates) have been used in substitution reactions with organic halides to build the prostaglandin skeleton [1038, 1039]. The approach can also be used to synthesize trichotecens by alkylating organotin enolates with cationic cyclohexadienyl iron complexes [1040]. The alkylation can occur via a free radical S_H2' process as used in a synthesis of 1,4-dicarbonyl compounds [1041]:



An interesting method for obtaining tin enolates consists of the opening of diketene by organotin alkoxide [1042] or tributyltin oxide [1043]. Mono- and dialkylated acetones have been efficiently obtained using this method (Scheme 9.3):

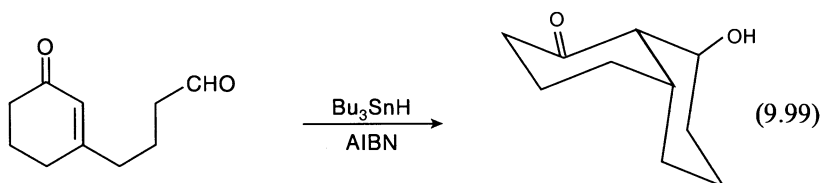


Scheme 9.3

An effort has been made to control the regioselectivity in the reaction of tin

enolates with α -halogenocarbonyl compounds, which can also react at the carbonyl bond, as shown in the next section. Additives were found, such as HMPT, Bu_3PO or Bu_4NBr , which allow the high-yield synthesis of 1,4-dicarbonyl compounds [1044]. In fact, five-coordinated tin enolates are involved and the reaction can be extended to other cases such as the transformation of α -haloimines into γ -iminoketones [1045] and, without any additive, to the reactions of tin enolates derived from diketene [1046].

In addition reactions. The capacity of tin enolates to add to carbonyl bonds is well illustrated by the intramolecular aldol-type reaction of a tin enolate, arising from the free radical 1,4-hydrostannation of an α -enone, under neutral conditions [1047]:

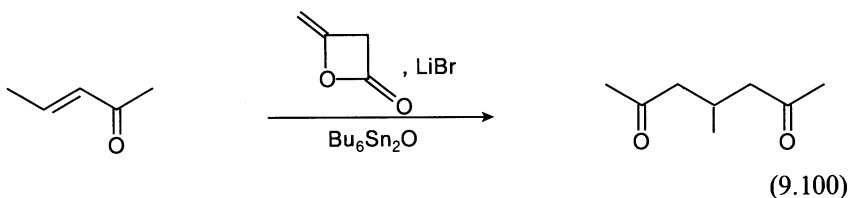


In addition, the already mentioned production of tin enolates from diketene has been applied to aldol reactions leading to α,β -unsaturated ketones [1048].

The control of diastereoselectivity has been studied in detail. While in general *syn* selectivity is observed, surprisingly enolates derived from 4-thianone react with aldehydes in a highly selective *anti* process [1049]. Similarly, enolates derived from chiral haloacetyl oxazolidinones react with aromatic aldehydes with *anti* diastereoselectivity via chelation control [1050]. On the other hand, enantiomerically pure *syn* aldols have been obtained by means of the Oppolzer's bornane sultam approach [1051].

The question of regioselectivity in the case of α -halo carbonyl compounds has been already approached in the previous section. Highly regio- and stereoselective additions to carbonyl bonds can be produced in the case of α -chloro cyclohexanones, by the use of tetraphenylstibonium bromide as catalyst [1052]. This additive and also five-coordinated organotin bromides, can promote addition to the carbonyl group, followed by elimination of tributyltin halide, to give epoxides [1053].

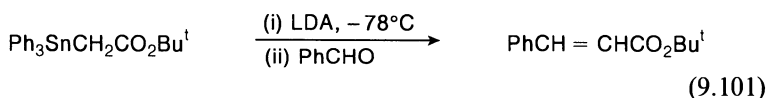
The organotin enolates, obtained from diketene, enter easily into Michael additions [1054]:



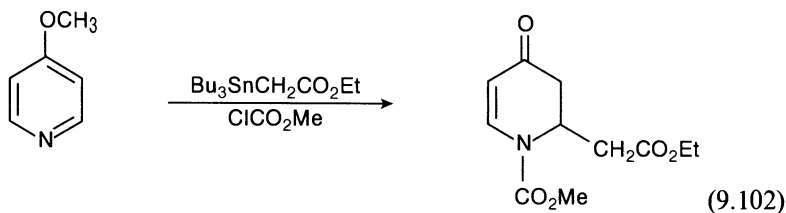
Also, diastereoselective Michael additions to crotonic acid derivatives have been described [1055]. Finally, following a different mechanistic route, but reaching a similar result, intramolecular free radical-promoted Michael additions have been observed via *O*-stannyl ketyls obtained by hydrostannation processes [1056]:

The case of α -stannyl esters or amides. Although in this case the equilibrium between *O*- and *C*-metallated species lies almost completely towards the *C*-stannylated species, these compounds will be considered as 'enolates' since the easy cleavage of the Sn–C bond leads to compounds expected by reaction of the Sn–O bond of the other isomer. α -Stannyl esters enter into Pd-catalyzed cross-coupling reactions with aryl halides, with asymmetric inductions in the case of the synthesis of alkyl 2-arylalkanoates in the presence of chiral ligands [1057]. Also, free radicals, which are able to add to electron-rich olefins like silyl enol ethers, are generated from α -stannyl esters and amides by oxidation with Ce(IV) salts [1058].

Addition reactions of the Reformatsky type are well documented. Thus, the synthesis of β -hydroxyesters by Lewis acid-catalyzed addition of α -stannyl esters to aldehydes or acetals is possible [1059], in some cases with high *syn* stereoselectivity [1060]. The same is true for the addition to aldimines which lead to β -aminoesters [1061]. α,β -Unsaturated esters can be directly obtained under basic conditions [1062]:



In a related way, α -stannyl esters have been entered into transmetallation reactions with chiral boron halides, to provide chiral boron enolates, subsequently submitted to an enantioselective and diastereoselective Reformatsky-type reaction [1063]. Without any transmetallation step, chiral oxazolidines were reacted (as their isomeric imino forms) to provide an enantiospecific synthesis of β -aminoesters [1064]. Finally, ethyl tributylstannylacetate has been more efficient than the traditional Reformatsky reagent for the carboethoxymethylation of functionalized pyridines, previously activated as acylpyridinium salts [1065]:

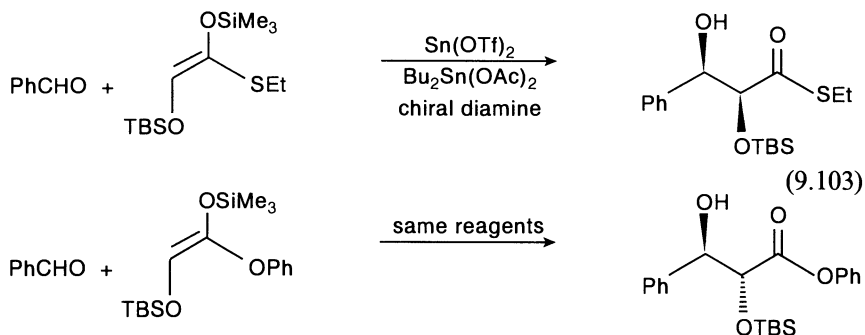


In addition, it is worth mentioning that aldol-type condensations occur from α -stannylated phosphonates and constitute an efficient route to (*E*)- or (*Z*)- α -alkenylphosphonates [1066].

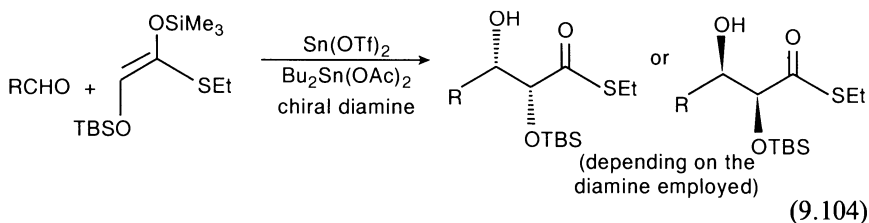
Tin(II) enolates. The possibility of generating tin(II) enolates from enolizable carbonyl compounds and stannous triflate, $\text{Sn}(\text{OTf})_2$, is at the origin of a large number of synthetic applications, especially linked to the capacity of the tin atom to expand its coordination. For instance, chiral tin(II) enolates, prepared from chiral amides, have been used in asymmetric aldol-type reactions with aldehydes [1067] or iminium species [1068]. Non-chiral thioamides, in the presence of chiral amines as ligands, lead to highly diastereo- and enantioselective condensations [1069]. Chiral ketones can similarly be transformed into useful chiral tin(II) enolates giving very selective stereocontrol [1070]. The $\text{Sn}(\text{II})$ enolate can also be prepared by Michael addition of RSSnOTf catalyst onto α,β -unsaturated ketones [1069].

However, a variety of impressive results have been reported by the Mukaiyama–Kobayashi group by using catalytic amounts of the Lewis acid $\text{Sn}(\text{OTf})_2$, chiral diamines and silyl enol ethers which can provide, by exchange, the reactive asymmetrically complexed $\text{Sn}(\text{II})$ enolates. Some recent data are particularly worth mentioning. Thus achiral ketene silyl acetals of acetic acid give very high enantiomeric excesses in aldol-type reactions with achiral aldehydes, in the presence of stannous triflate, tributyltin fluoride and a chiral diamine [1071]. Similar results are obtained from silyl enol ethers of *S*-alkyl ethanethioates with aldehydes [1072, 1073].

In the presence of diacetoxydibutyltin as additive, a very efficient control of diastereoselectivity and enantioselectivity, with *ee* >90%, was observed, depending on very small differences in the structure of the silyl enol ether [1074]:



Both *syn* or *anti* diastereoisomers can also be obtained, from the same substrates and reagents, depending on the catalysts or the chiral diamine employed [1075, 1076]. Even more impressive is the highly selective synthesis of both enantiomers, with only minute changes in the chiral auxiliary [1077]:



Finally and less surprisingly, it was found that both diastereoisomers can be prepared by using either the (*E*)- or the (*Z*)-silyl enol ether [1078, 1079].

9.3.3 Reactions of organotin halides and cyanides

Tin halides behave as very good catalysts for etherification, transketalization [1080, 1081] and cleavage of ketals [1082]. In the presence of trimethylsilyl chloride, tin(II) chloride cleaves *p*-methoxybenzyl ethers selectively in the presence of benzyl ethers [1083].

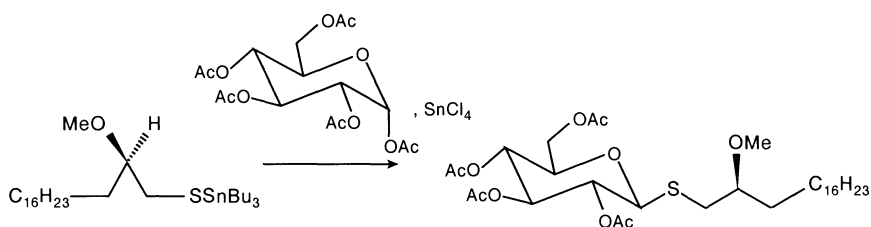
Tin cyanide reacts with α -chiral aldehydes to give the corresponding cyanohydrins with a very high diastereoselectivity and with better results than the corresponding silicon compound [1084]. When used as a catalyst, tin cyanide promotes the conversion of aldehydes to acylated cyanohydrins with acetyl cyanide [1085].

9.3.4 Reactions of organosilyltins

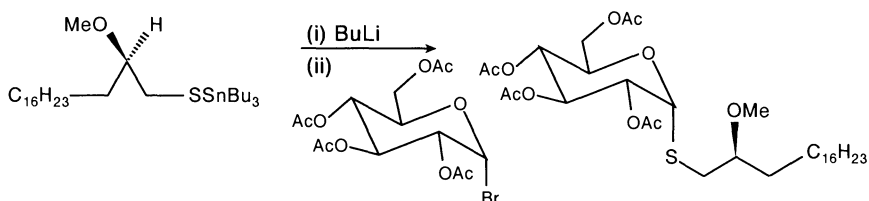
Intramolecular coupling of vinyl triflates with aryl halides proceeds smoothly in the presence of trimethylsilyltributyltin and a palladium catalyst [1086]. Fluorine anion activates the same tin reagent and allows the generation of stannyl anions. When opposed to an ω -amidovinyl halide, transmetallation occurs leading to cyclized products formed by addition of the vinyl moiety to the amidocarbonyl [1087]. This reaction led to a short synthesis of (–)-cephalotaxine [1088].

9.3.5 Reactions of organotins with sulfur– or selenium–tin bonds

Classical synthesis of sulfides by coupling halides and tin sulfides has been extended to alkenyl [1089] and aromatic [1090, 1091] halides by using palladium catalysts. It is used in a synthesis of chuangxinmycin methyl ester [1091]. Both anomers of thioglycosides are selectively obtained by the coupling of an alkylthiotin with glucoside derivatives, either in the presence of tin tetrachloride or after a transmetallation leading to an alkylthiolate [1092, 1093]:



(9.105)



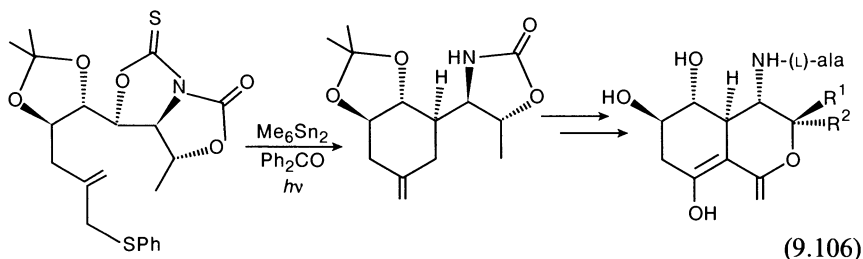
The same reactions conducted with alkylselenotins give selenoethers [1094].

In the presence of Lewis acid, acetals react with bis(alkylthio)tins to give monothioacetals while aldehydes lead to dithioacetals. Acetals of enals are converted under the same conditions into γ -alkoxy allyl sulfides [1095]. Tetrahydropyranyl ethers, which are unsymmetrical acetals, are cleaved to give alcohols on exposure to thiostannanes. It is a mild method of deprotection of alcohols where silyl, acetyl and methoxymethyl groups are tolerated [1096].

Treatment of bis(trialkyltin)sulfides and -selenides with halides provides the corresponding symmetrical chalcogenides in good yields when a fluoride source is used to promote the substitution reaction [1097, 1098]. Diacyl chlorides are reactive enough to couple with stannadithiane without catalyst. Macrocyclic poly(thialactone)s are then obtained [1099]. Selenoaldehydes [1100] or thioketones [1101] are obtained when *gem*-dichlorides or ketones are treated with bis(tributyltin)selenide or bis(tributyltin)sulfide, respectively. Sodium dithiocarbamates are obtained from amines, carbon disulfide and bis(tributyltin)oxide, even in the presence of hydroxyl groups [1102]. Reductive properties of tin sulfides are used in the transformation of azides to oximes, nitro compounds to hydroxylamines [1103] and trisulfides to disulfides [1104]. When treated with thionyl chloride, dithiastannoles are a good source of trithioles [1105]. With esters, they lead to fulvalenes [1106]. Facile cleavage of the tin-sulfur bond leads to interesting applications. In the presence of bis(tributyltin)oxide and of catalytic amounts of AIBN, thiols add to alkenes through tin sulfides. Hydroxyl and acid groups are tolerated [1107]. Under irradiation, tin dithiocarbonates undergo radical fragmentation leading to organodithiocarbonates after reaction with organic halides [1108].

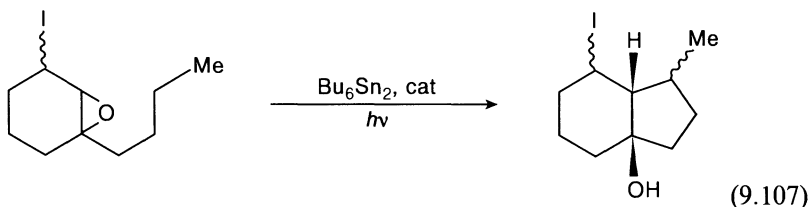
9.3.6 Reactions of hexaorganoditins

Most of the studies on hexaorganoditins have been conducted with hexabutylditin. They concern radical reactions where the ditins show the advantage over tin hydrides of creating carbon radicals without transferring hydrogen atoms. That allows coupling processes and skeleton rearrangement to occur. Coupling processes are exemplified in the reaction of α -substituted glycine derivatives with hexabutylditin. When treated under radical conditions without suitable partners, dimerization products are obtained [1109], while in the presence of disulfides, α -alkylthio-substituted glycines are obtained under the same conditions [1110]. Reaction between allyl bromides and allyl sulfides leads to a selective synthesis of 1,5-dienes without formation of homocoupling compounds [1111]. Intramolecular couplings are also powerful tools for annulations which are characterized by a high level of stereoselectivity. ω -Heterosubstituted allyl sulfides undergo a 6-*endo*-trig radical cyclization [1112] giving methylenecyclohexanes exemplified in a synthesis of (+)-actinobolin [1113]:



Ditins are also useful to generate radicals involved in addition processes. Suitable partners can be nitrites [1114] or isonitriles [1115] which lead to oximes or imines, respectively. With ω -unsaturated isonitriles rearrangement of the imino-radical intermediate allows cyclizations to take place [1116]. They have been used in a synthesis of anticancer camptothecin [1117]. When cyclopropanes and vinylsulfones [1118] or ω -unsaturated halides [1119] are used, polycyclic compounds are obtained. Under suitable conditions, rearranged radicals formed from ω -unsaturated iodides and ditins can be trapped by tin iodide instead of abstracting hydrogen to the solvent. In this case, iodides are the product of this atom transfer reaction [1120]. Five-, six- or seven-membered rings form selectively, depending on chain length and unsaturation substitution [1121]. Optically active ω -unsaturated α -iodosulfams [1122] or amides [1123] give high levels of asymmetric induction, which have been turned into account in a synthesis of (–)-trachelanthamidine [1123]. With ω -unsaturated iodolactones, a combination of inter- and intramolecular additions leads to macrocyclic lactones, selectively [1124], while with the corresponding lactams only intramolecular addition is observed

[1125]. α -Epoxy iodides give cyclized β -iodo alcohols under atom transfer conditions [1126].



High affinity of tin towards sulfur is used in a synthesis of tetrathiafulvalenes by the reductive dimerization of a thiocarbonate by hexabutylditin [1127]. The reducing properties of hexabutylditin allow its use instead of zinc in Reformatsky-type reactions, providing that dibutyltin diiodide is used as catalyst [1128]. Transfer reactions are not limited to iodides. They are also efficient with ω -unsaturated selenides [1129].

Polymer-supported ditins have been demonstrated to show the same properties as free ditins. They allow an easy removal of organotin by-products [1130].

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10 Recent studies on the mode of biological action of di- and trialkyltin compounds

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10.1 Introduction

Organic tin compounds are characterized by the presence of at least one covalent carbon–tin bond. The compounds have a tetravalent structure and are classified as mono-, di-, tri- and tetraorganotins depending on the number of alkyl and aryl moieties. The anion is usually chloride, fluoride, oxide, hydroxide, carboxylate or thiolate.

The biological activity of organotins is essentially determined by the number and nature of the alkyl or aryl groups bound to tin, whereas the nature of the anionic group is only of secondary importance. The tetra-, tri-, di- and monoorganotins display remarkable differences in biological activities. Trialkyl- and triaryltin derivatives exert a powerful toxic action on the central nervous system [1–22]. Within the series of trialkyltin derivatives, the lower homologs such as trimethyltin and triethyltin are the most toxic when given orally and the oral toxicity diminishes progressively from tri-*n*-propyltin to tri-*n*-hexyltin with tri-*n*-octyltin being non-toxic. Tetraalkyltins resemble trialkyltins in their biological activity, but their effects are often less severe and delayed. This has been explained by the conversion of tetra- into trialkyltin compounds *in vivo* [23–25]. Monoalkyltins do not produce any important toxic action [26]. The dialkyltin compounds from methyl to hexyl induce bile duct lesions in rats and mice but not in rabbits or guinea pigs [27]. Further, dialkyltins such as dibutyltin and dioctyltin induce thymus atrophy, and their effects on the immune system constitute the most sensitive criteria of their toxicity [28–43].

In general, an alkyltin compound is much more toxic when it is given intraperitoneally (i.p.) than when given orally. However, triethyltin and trimethyltin are exceptions to this rule. This difference in toxicity results from the fact that, except for the dimethyl-, trimethyl- and triethyltin compounds, the alkyltin compounds are not absorbed very well from the gastrointestinal tract.

In this article the mode of biological action of di- and trialkyltin compounds is reviewed with a focus on the connection with immunity and the nervous system.

10.2 Neurotoxicity

Earlier reports indicate that of all alkyltin derivatives, neurotoxic effects are limited to trialkyltin derivatives such as trimethyltin and triethyltin. No signs of neuronal damage or edema are observed in the brain of animals treated with dialkyltin derivatives or any of the higher trialkyltin homologs [1–3].

10.2.1 Brain lesions

The lower alkyltins, which produce a variety of brain lesions, such as trimethyltin and triethyltin, are found to be extremely potent neurotoxicants with triethyltin being primarily a myelinotoxicant [44, 45] and trimethyltin a neuronotoxicant [11–15, 46–48].

Triethyltin derivatives exert a powerful toxic action on the central nervous system. The compounds produce a diffuse hemorrhagic encephalopathy [4] and a generalized progressive weakness that ends in death [5] as the acute symptoms, and further an interstitial edema confined to the white matter of the brain [4] as the chronic symptoms. The basic pathological lesion of this edema is limited to myelin. The myelin sheaths are dilated and filled with fluid. Neonatal exposure to triethyltin causes a reduction of brain weight and delayed myelinogenesis, but no cerebral edema is observed [6]. Consequently, adult electrophysiological alterations [7], deviation from neurobehavioral function [8] and neuromorphological alterations [9] are observed.

Trimethyltin derivatives have the same order of neurotoxicity as the triethyltin derivatives. The neurological effects of trimethyltin are tremor [10, 26], hyperexcitability [10, 26], aggressiveness [10, 26], necrosis of neurons in the hippocampus and the pyriform cortex [1, 11], neuronal damage in the amygdaloid nucleus, brain stem neurons, neocortex, spinal cord, sensory neurons and retina [12–17], selective vulnerability of the hippocampus [12–17], and behavioral and neuropathological alterations [18, 19]; however, no cerebral edema is found, in contrast to triethyltin. Particularly in humans, a variety of psychomotor changes, including irritability, depression, aggressiveness, headaches, tremors, convulsions and changes in libido [20, 21] are observed.

Although tripropyltin and tributyltin derivatives produce brain edema, their neurological effects are much less than those associated with triethyltin derivatives when given orally [10, 22].

However, we recently demonstrated that these compounds produce a variety of brain lesions at the same toxic level as trimethyltin and triethyltin when they are given intraperitoneally [24, 25, 49–59]. This is only a reflection of their poor absorption, that is, lower alkyltin compounds are readily absorbed from the gut, however, there are differences between species in the degree of absorption.

10.2.2 *Hippocampal lesions*

As described in section 10.2.1, while triethyltin is primarily myelinotoxic, inducing swelling and vacuolar changes in the central myelin [44, 45], trimethyltin is found to be neuronotoxic, leading to extensive neuronal changes and necrosis in a number of brain areas, including the limbic system and particularly the hippocampus [1, 11, 13, 14, 47].

In particular trimethyltin produces a selective pattern of neuronal damage that is most evident in the hippocampus [1, 11]. Within the hippocampus, loss of pyramidal cells primarily in CA1 and CA3 is a conspicuous feature of trimethyltin toxicity [60–62]. Further, trimethyltin induces zinc depletion in the mossy fibers (region of CA3 and CA4) of the hippocampus formation, which contains more zinc than most other parts of the central nervous system [63]. In this connection, zinc plays an important role in the cellular basis of learning and memory as the modulator of increases in intracellular Ca^{2+} concentration mediated by glutamate receptor families [64–67], the voltage-dependent calcium channel (VDCC) [68], the ATP channel [69], etc.; as the modulator of protein phosphorylation by protein kinase C [70], calcium/calmodulin-dependent protein kinase II (CaM kinase II) [71], tyrosine kinase (Fyn) [72, 73], etc.; and as the modulator of retrograde messages [74, 75] by carbon monoxide (CO), nitric oxide (NO), etc., for induction and maintenance of long term potentiation (LTP) in the CA1 region of the hippocampus [76]. These results suggest that the antagonistic action or interaction of trimethyltin on zinc in the hippocampus may play an important role in trimethyltin toxicity, including impairment of learning and memory.

Recently, we demonstrated that other trialkyltins, particularly tributyltin, also produced a variety of hippocampal lesions similar to those of trimethyltin when the compound was given intraperitoneally.

Tributyltin was quickly distributed to the hippocampus after a single intraperitoneal administration and reached a maximum level within a day, decreasing during the subsequent 3 day period (Figure 10.1) [24, 25, 49–51, 77]. In addition, the tributyltin exposure induced an excessive increase in the concentration of calcium in the hippocampus (Figure 10.1). These results suggest that the excessive increase (or accumulation) of calcium induces severe neuronal damage (or cell death) in the hippocampus [49–51, 54, 55].

10.2.3 *Impairment of sensory organs*

Trialkyltins induce dysfunctions in the visual [78, 79], auditory [80–82], olfactory [51, 54–58] and somatosensory [83] systems. Earlier morphological studies revealed that trimethyltin was not only a central nervous system neurotoxicant (e.g. the olfactory cortex) but is also toxic to certain neurons in the peripheral nervous system (e.g. forsal root ganglia) and to special sensory organ neurons in the inner ear and the retina [16].

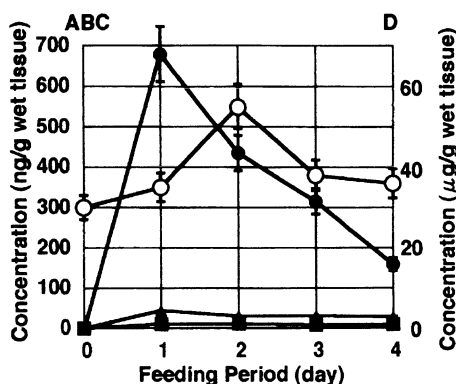


Figure 10.1 Movements of tributyltin and its metabolites in the hippocampus of rats injected single-intraperitoneally with tributyltin chloride (2.5 mg kg^{-1} body weight). Vertical bars denote the SE of the mean for five determinations. Tributyltin (●, A), dibutyltin (▲, B), monobutyltin (■, C), calcium (○, D).

Recently, we found that, in addition to trimethyltin, other trialkyltins, particularly tributyltin, impaired the sensory organs when the compound was given intraperitoneally [51–55]. In particular, tributyltin produced damage and neuronal destruction in the pyriform and olfactory cortices after intraperitoneal exposure (Figure 10.2). Extensive necrosis and cell loss were observed in the areas of the olfactory tubercle (olfactory cortex) and pyriform cortex which normally contain many small granule neurons [51, 53, 54]. Further, the tributyltin induced an excessive accumulation of calcium in the olfactory bulb (section 10.4.5).

These results suggest that the abnormal calcium accumulation induces severe destruction of the cortical neurons of the olfactory bulb [51, 53–58].

10.3 Immunotoxicity

10.3.1 Immunosuppression

Various immune function studies have indicated that cell-mediated immunity and T cell-dependent humoral immunity are suppressed by dialkyltin exposure [34, 84]. A dose-related suppression of cell-mediated immunity occurs in such manifestations as tuberculin hypersensitivity, skin graft rejection, graft-versus-host reactivity and lymphocyte transformation by the T-cell mitogen, that is, phytohemagglutinin (PHA) and concanavalin A (Con A). The resistance against *Listeria monocytogenes* also a T cell-dependent phenomenon, decreased with dose (Table 10.1) [31, 35–37].

Triorganotin compounds such as tributyltin and triphenyltin also suppress the thymus-dependent immune responses. However, possible immunotoxic

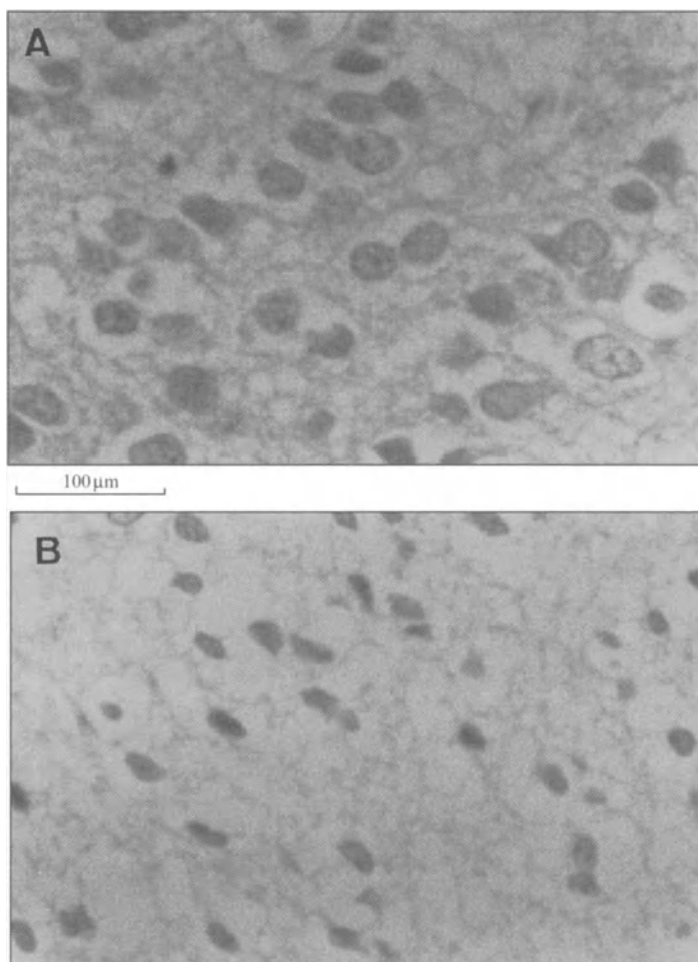


Figure 10.2 Olfactory cortex, (A) control, (B) tributyltin-treated, 3 days. Extensive destruction of the cortical neurons was observed.

properties of trimethyltin or triethyltin compounds may be overshadowed by their neurotoxicity [3]. For the higher trialkyltin homologs only slight (trihexyltin) or no effect (trioctyltin) on the thymus is observed.

10.3.2 *Thymus atrophy*

Dibutyltin, dioctyltin and tributyltin compounds cause severe thymus atrophy (Table 10.2) [32–43, 85–88]. This atrophy is reversible (Figure 10.3) [28–31, 35–43], however, and its degree correlates with the concentration of organotin in the thymus (Figure 10.4) [41, 42, 87]. At histopathological exam-

Table 10.1 Effects of dialkyltin compounds on the immune functions of rats

Cell-mediated immunity	Effect ^a
<i>In vivo</i>	
delayed-type hypersensitivity to tuberculin	+
allograft rejection	+
graft-versus-host reaction	+
resistance to <i>Listeria monocytogenes</i> infection	+
<i>In vitro</i>	
lymphocyte transformation by phytohemagglutinin (PHA) and concanavalin A (Con A)	+
<i>Humoral immunity</i>	
<i>In vivo</i>	
thymus-dependent antibody synthesis to sheep red blood cells (SRBCs)	+
thymus-independent antibody synthesis to <i>E. coli</i> lipopolysaccharide (LPS)	–
<i>In vitro</i>	
plaque formation against SRBCs	+
transformation of lymphocytes by LPS	–
Phagocytosis by macrophages of carbon particles	–
Sensitivity to LPS	+

^a+ Denotes a suppressive effect on immune parameters or an increase of susceptibility to infection or *E. coli* LPS; – = no effect.

Table 10.2 Relative organ weights of rats fed various organotin compounds (percentage of controls)

	Body weight	Thymus	Adrenal	Liver	Spleen	Kidney	<i>N</i>
Bu ₂ SnCl ₂	97	48***	125	93	98	96	6
Bu ₃ SnCl	90	58***	132*	93	75*	86*	7
BuSnCl ₃	95	106	116	91	89	106	6
Bu ₄ Sn	101	88	119	89	79*	96	6
Pr ₂ SnCl ₂	84	89	98	82**	88	97	7
Me ₂ SnCl ₂	96	92	97	85*	112	99	6
MeSnCl ₃	105	85	103	101	92	100	6
OC ₂ SnCl ₂	101	39****	100	104	116	100	7
Ph ₃ SnCl	91	100	113	89*	87	99	6
SnCl ₄	88	83	110	92	73**	103	6

Note: Wistar-derived weanling rats (males, 40–45 g) fed independently 100 ppm organotin for 10 days. All values are the mean of 6–7 animals; those marked with asterisks differ significantly (Student's *t*-test) from the corresponding control value: **p* < 0.05, ***p* < 0.02, ****p* < 0.01, *****p* < 0.001.

ination, there is marked depletion of lymphocytes in the thymic cortex rather than in the thymic medulla (Figure 10.5). Furthermore, cortisone pretreatment studies reveal that immature cells in the thymic cortex are far more sensitive to organotin compounds than mature cells [35–42, 89, 90]. DNA synthesis of the thymic lymphocytes is significantly inhibited by dibutyltin and dioctyltin compounds at a concentration of 10^{–7} M, at which cell viability is not yet impaired (Figure 10.6). Moreover, a parallel is found to exist between dose–response curves of dialkyltin for DNA synthesis and cell viability. These results indicate that organotins primarily induce inhibition of cell proliferation and secondly cause cell death [36, 37, 41, 42, 91, 92].

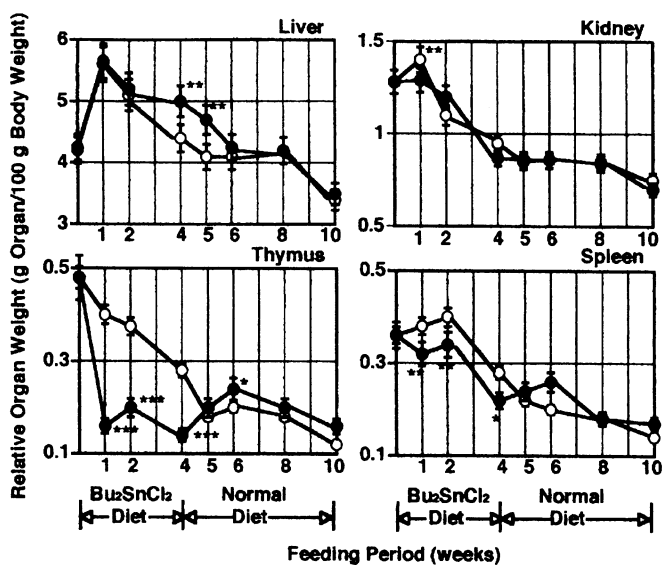


Figure 10.3 Relative organ weights of rats fed 0 or 100 ppm dibutyltin dichloride (Bu_2SnCl_2) for 4 weeks and after that period a normal diet for 6 weeks. Vertical bars denote the SE of the mean for ten determinations; those marked with asterisks differ significantly (Student's *t*-test) from the corresponding control value: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. (O) Control (0 ppm) group, (●) 100 ppm group.

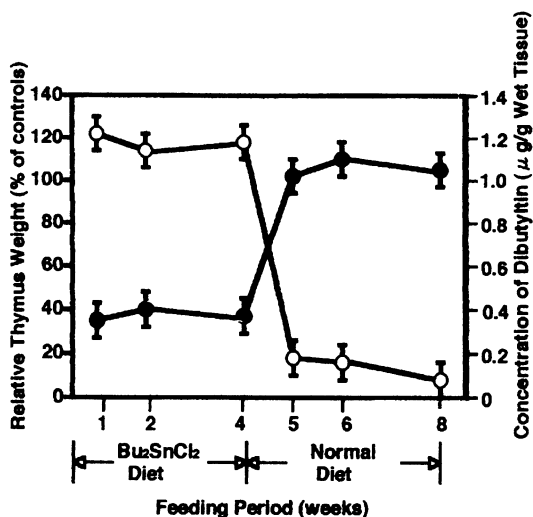


Figure 10.4 Relationship between thymus atrophy and the concentration of dibutyltin in the thymus of rats fed 100 ppm Bu_2SnCl_2 for 4 weeks and after that period a normal diet for 6 weeks. (O) Concentration of Bu_2SnCl_2 in the thymus ($\mu\text{g g}^{-1}$ tissue), (●) relative thymus weights are given as percentages of control values. Vertical bars denote the SE of the mean for ten determinations.

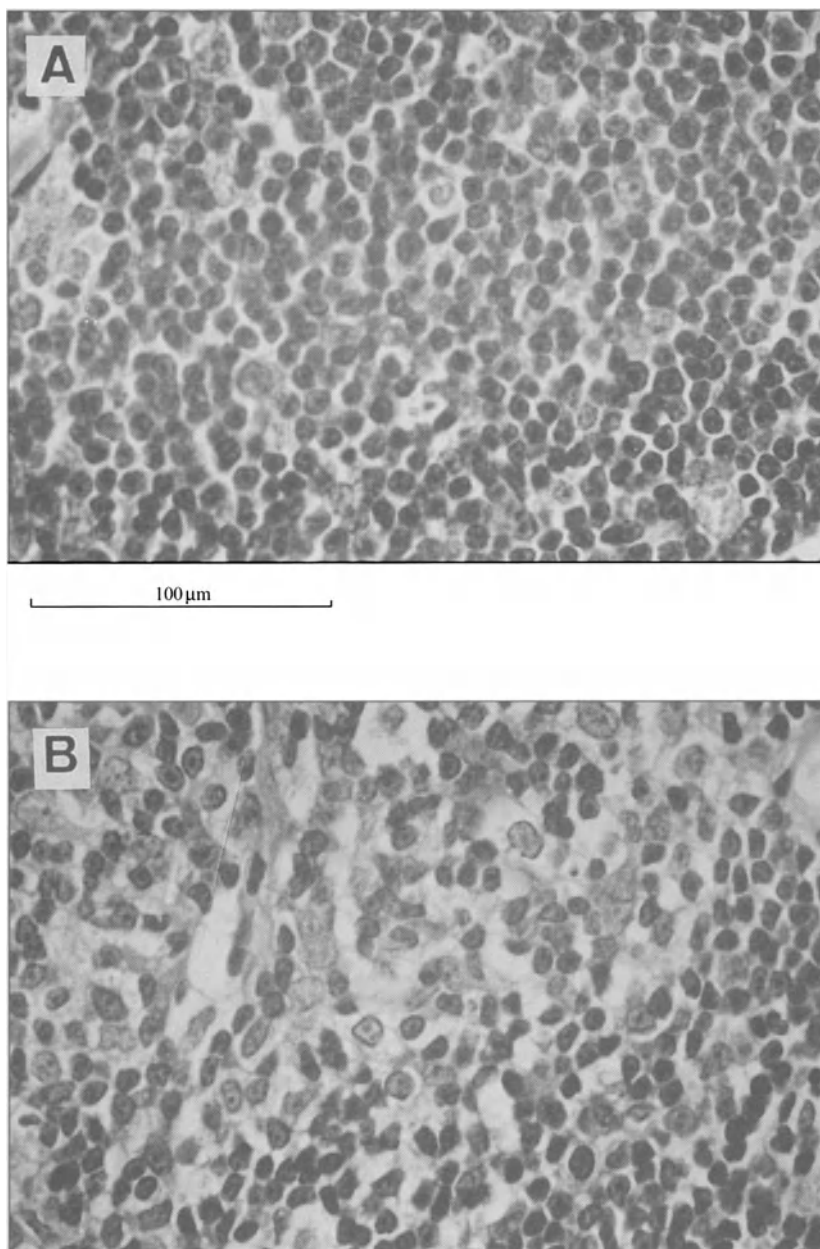


Figure 10.5 Part of thymic cortex from a control rat (A) and a rat (B) fed 100 ppm dibutyltin dichloride (Bu_2SnCl_2) for 2 weeks. Note the complete lymphocyte depletion of the cortex (B). Hematoxylin and eosin.

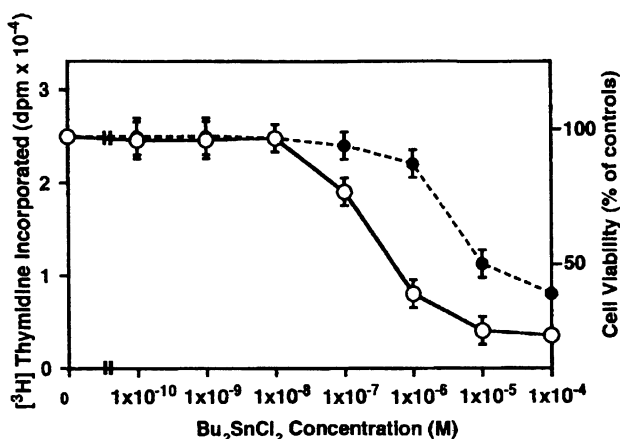


Figure 10.6 Effect of Bu_2SnCl_2 concentrations on DNA synthesis (O) and viability (●) of rat thymocytes. Cells (10^6 cells ml^{-1}) were cultured in triplicate during 24 h and [^3H]-thymidine was present during the last 4 h of the culture period. Vertical bars denote the SE of the mean for seven determinations.

10.3.3 Changes in the membrane surface antigens of T cells

As described above, organotin compounds such as dibutyltin dichloride induce severe, reversible and dose-dependent thymus atrophy and immunodeficiency. These results suggest that the organotins may have an effect on the differentiation and maturation of T cells in the thymus. In this regard, changes in the membrane surface antigens of T cells of SPF Wistar-derived rats which developed symptoms of atrophy in the thymus were analyzed with a fluorescence activated cell sorter (FACS can), using a monoclonal antibody against each cell surface determinant (Table 10.3).

Table 10.3 Cell surface marker analysis of thymocytes and peripheral T cells of organotin-exposed rats

Lymphocyte subpopulation	Relative count (%) ^a			
	Control	Thymocytes Organotin-exposed	Peripheral T cells Control	Peripheral T cells Organotin-exposed
Thy 1.1 (MRC OX-7)	99.42 ± 0.19	98.58 ± 0.57*	38.90 ± 2.20	32.84 ± 1.68**
CD2 (MRC OX-34)	99.60 ± 0.15	99.44 ± 0.15	85.72 ± 3.97	78.98 ± 6.92
Alpha/Beta (R73)	80.26 ± 2.03	61.72 ± 2.12***	98.50 ± 0.84	97.60 ± 1.05
CD4 (W 3/25)	4.50 ± 0.91	5.48 ± 1.55	48.41 ± 2.28	48.75 ± 3.06
CD4, CD8 double-positive	88.72 ± 1.11	77.12 ± 6.54**	6.57 ± 6.04	3.29 ± 0.97*
CD4, CD8 double-negative	1.35 ± 0.19	6.90 ± 2.64**	30.30 ± 4.78	34.97 ± 3.87
CD8 (OX-8)	5.11 ± 0.79	10.50 ± 2.55**	14.73 ± 2.41	12.94 ± 1.43

^aThe values are the mean ± SE of 5 Wistar-derived weanling rats (males, 40–45 g) per group. After 10 days of feeding with NMF solid diet containing 100 ppm Bu_2SnCl_2 (Oriental Yeast Co. Ltd), cell suspensions were made of the thymus and peripheral blood cells, and lymphocyte subpopulations were analyzed on a fluorescence-activated cell sorter (FACS) with monoclonal antibodies to rat cell surface determinants. The clones of antibodies used are indicated between parentheses. Those marked with asterisks differ significantly (Student's *t*-test) from the corresponding control value: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

The dibutyltin-exposed thymocytes revealed significant decreases in the percentage of α/β (T cell receptor) antigen cells and CD4 and CD8 double-positive cells (undifferentiated cells), and increases in the percentage of CD4 antigen cells (rat T helper cells and macrophages) and CD8 antigen cells (rat T suppressor/cytotoxic cells). In the peripheral T cells, decreases in the percentage of Th1.1 antigen cells (total T cells), CD2 antigen cells (E rosette forming cells) and CD4 and CD8 double-positive cells were observed [93–95]. These data indicate that the immunodeficiency induced by organotins is manifested as T cell dysfunction, which is caused not only by quantitative changes in the T cells such as thymus atrophy but also by qualitative changes in the T cells, such as changes in their membrane surface antigens, specifically, impairment of the process of differentiation and maturation of T cells in the thymus.

10.3.4 Antitumor activity of organotins

We investigated the antitumor activity of organotin compounds *in vivo* towards various tumor systems (Table 10.4). As a result, Bu_2SnCl_2 was found to exhibit reproducible activity *in vivo* towards Ehrlich ascites tumor, IMC carcinoma, P-388 lymphocytic leukemia and sarcoma 180 systems, in descending order of activity. In particular, the compound showed the highest activity against the Ehrlich ascites tumor system and gave a T/C value (life span) in the range of 98 to 186, with the dosage ranging from 0.1 to 3.0 mg kg^{-1} , the maximum activity in the present case being observed at a single dose of 3 mg kg^{-1} . Generally, a total of one to two injections of high-dose levels ($2\text{--}3 \text{ mg kg}^{-1}$), at which the compound does not show any toxicity, were more effective against any tumor than five low-dose injections ($0.1\text{--}0.3 \text{ mg kg}^{-1}$) [28–30, 92, 96–99].

Figure 10.7 indicates the antitumor effect of dibutyltin on Ehrlich ascites tumor cells. The survival period of the control group was about 22 days. An increase in survival was observed upon administration of dibutyltin. In particular, a total of one to two injections of high-dose levels was more effective against the tumor cells than five low-dose injections [28–30, 92, 96, 99–101].

Table 10.5 presents the effect of dibutyltin on tumor initiation–promotion systems in mouse skin carcinogenesis. When the optimal dose of dibutyltin was presented at the first phase TPA promotion stage (stage I promotion) of the two-stage promotion system, the most effective inhibitory effect was obtained. In particular, when $5 \mu\text{g}$ of dibutyltin was given at the TPA promotion stage, the occurrence of papillomas was completely suppressed (Figure 10.8) [28–30, 92, 96, 100, 102–106].

Figure 10.9 demonstrates the effect of dibutyltin on two-stage *in vitro* transformation of BALB/c 3T3 cells. The cells were initiated with MCA and promoted with TPA. Dibutyltin was added at approximately the same time

Table 10.4 Screening data for antitumor activity of dibutyltin compound

Tumor	Dose ^a		Life span ^b	
	mg kg ⁻¹ i.p.	Injection time	Survival time (days)	T/C (%)
Sarcoma 180	0	5	15.1±0.4	100
	0.1	5	17.6±0.3	117
	0.3	5	17.8±0.4	118
	1.0	5	15.8±0.5	105
	2.0	2	15.0±0.3	100
	2.0	4	15.0±0.4	100
	3.0	1	13.2±0.3	87
	3.0	2	13.0±0.3	86
IMC-carcinoma	0	5	16.5±0.3	100
	0.1	5	18.6±0.4	113
	0.3	5	19.1±0.5	116
	1.0	5	19.8±0.5	120
	2.0	2	20.8±0.3	126
	2.0	4	21.3±0.7	129
	3.0	1	21.0±0.6	127
	3.0	2	22.0±0.7	133
Lymphocyte leukemia P-388	0	5	10.4±0.3	100
	0.1	5	10.6±0.2	102
	0.3	5	12.1±0.5	116
	1.0	5	11.8±0.4	114
	2.0	2	12.3±0.5	118
	2.0	4	12.2±0.5	117
	3.0	1	12.1±0.3	116
	3.0	2	12.5±0.3	120
Ehrlich ascites tumor	0	5	21.1±0.4	100
	0.1	5	20.7±0.5	98
	0.3	5	21.8±0.7	104
	1.0	5	22.7±0.5	108
	2.0	2	29.1±0.4	138
	2.0	4	28.1±0.8	133
	3.0	1	39.3±0.7	186
	3.0	2	37.6±0.7	178

^aA total of one to five injections were given at daily intervals in each experiment.

^bThe increase in survival of treated animals over controls is expressed as T/C (%). The values of survival time are the mean ± SE of 10 animals per group.

as MCA or TPA. Line A represents the entire negative control, while line B represents the case of MCA treatment alone, that is, initiation treatment only. Line C represents the case of TPA treatment alone, namely promotion treatment only. Under these conditions the cells do not transform. However, when the cells were initiated with MCA and promoted with TPA, as in line D, the cells were transformed completely. This represents positive control. On the other hand, when 300 nM (3×10^{-7} M) of dibutyltin existed at the MCA initiation stage (line E), the transformation was completely suppressed. Conversely (line F), when the same amounts (3×10^{-7} M) of dibutyltin existed at the TPA promotion stage, the transformation was not suppressed. When a low concentration (3×10^{-8} M) of dibutyltin was presented at the MCA initiation stage and TPA promotion stage, respectively (lines G and H), no

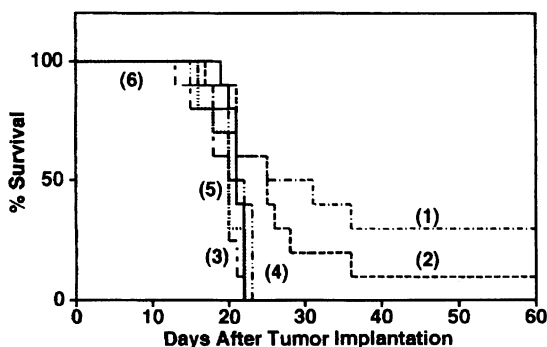


Figure 10.7 Antitumor effect of Bu_2SnCl_2 on Ehrlich ascites tumor cells. Bu_2SnCl_2 was injected i.p. into dd-Y mice daily from days 1 to 5 after Ehrlich tumor cells (5×10^6) were inoculated i.p. into the mice. Survival times are the means of 10 animals per group. (1) $3 \text{ mg kg}^{-1} \times 1$ or 2 (---), (2) $2 \text{ mg kg}^{-1} \times 2$ or 4 (----), (3) $1 \text{ mg kg}^{-1} \times 5$ (- · - · -), (4) $0.3 \text{ mg kg}^{-1} \times 5$ (- · · - ·), (5) $0.1 \text{ mg kg}^{-1} \times 5$ (.....), (6) controls (—).

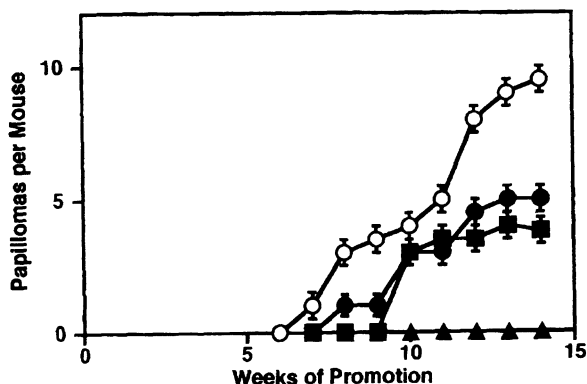


Figure 10.8 Inhibitory effect of Bu_2SnCl_2 on two-stage mouse skin carcinogenesis system of initiation and promotion. The mice were initiated with 100 nM of DMBA and promoted with $5 \mu\text{g}$ of TPA and $2.5 \mu\text{g}$ of mezerein. Bu_2SnCl_2 ($5 \mu\text{g}$) was applied 30 min before treatment with the initiator and promoters. Each point is expressed as papilloma number per mouse and vertical bars denote the SE of the means for ten animals per group. (O) controls, (●) DMBA- Bu_2SnCl_2 (initiation stage), (▲) TPA- Bu_2SnCl_2 (promotion stage I), (■) mezerein- Bu_2SnCl_2 (promotion stage II).

suppression of transformation was observed. These results verify that dibutyltin is a potent inhibitor of the MCA initiation stage in the two-stage cell transformation system (Figure 10.9) [28–30, 92, 96, 100, 102–106].

In contrast to the finding obtained from *in vitro* two-stage transformation studies, *in vivo* studies of two-stage mouse skin carcinogenesis systems consistently showed that dibutyltin effectively inhibited the TPA promotion stage. The reason for this apparent discrepancy between the *in vivo* and *in*

Table 10.5 Effect of Bu_2SnCl_2 on tumor initiation-promotion systems in mouse skin carcinogenesis

Initiation	Promotion		Tumor response % of positive controls in (Exp. 10)
	Stage I	Stage II	Papilloma (number/mouse)
1 Acetone	1 wk TPA	Mezerein	0
2 DMBA	1 wk Acetone	Mezerein	0
3 DMBA	1 wk TPA	Acetone	2.4±0.1
4 DMBA	1 wk TPA	Mezerein	9.6±0.3
5 DMBA + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	1 wk TPA + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	Mezerein + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	0
6 DMBA + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	1 wk TPA + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	Mezerein + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	16.8±0.7
7 DMBA + $\text{Bu}_2\text{Sn}(0.5 \mu\text{g})$	1 wk TPA	Mezerein	20.2±0.8
8 DMBA + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	1 wk TPA	Mezerein	5.6±0.2
9 DMBA + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	1 wk TPA	Mezerein	19.2±0.8
10 DMBA	1 wk TPA + $\text{Bu}_2\text{Sn}(0.5 \mu\text{g})$	Mezerein	2.9±0.1
11 DMBA	1 wk TPA + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	Mezerein	0
12 DMBA	1 wk TPA + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	Mezerein	3.8±0.2
13 DMBA	1 wk TPA	Mezerein + $\text{Bu}_2\text{Sn}(0.5 \mu\text{g})$	22.1±0.9
14 DMBA	1 wk TPA	Mezerein + $\text{Bu}_2\text{Sn}(5 \mu\text{g})$	4.5±0.2
15 DMBA	1 wk TPA	Mezerein + $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	15.4±0.7
16 - $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	1 wk - $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	- $\text{Bu}_2\text{Sn}(50 \mu\text{g})$	0

Initiation was with 100 nmol of DMBA (in Exp. 1, only acetone); 1 week later, twice-weekly applications of 5 μg of TPA or acetone were begun (Stage I). Starting on the third week of promotion, the mice received twice-weekly applications of 2.5 μg of mezerein or acetone (Stage II) for the rest of the 14-week experiment. Bu_2SnCl_2 was applied 30 min before treatment with the initiator or promoters. At the end of the experimental period, >95% of the mice were alive. Tumour response is expressed as the mean \pm SE of the papilloma number per mouse and as a percentage of the positive control (in Exp. 4). Each value is the result of 10 animals per group.

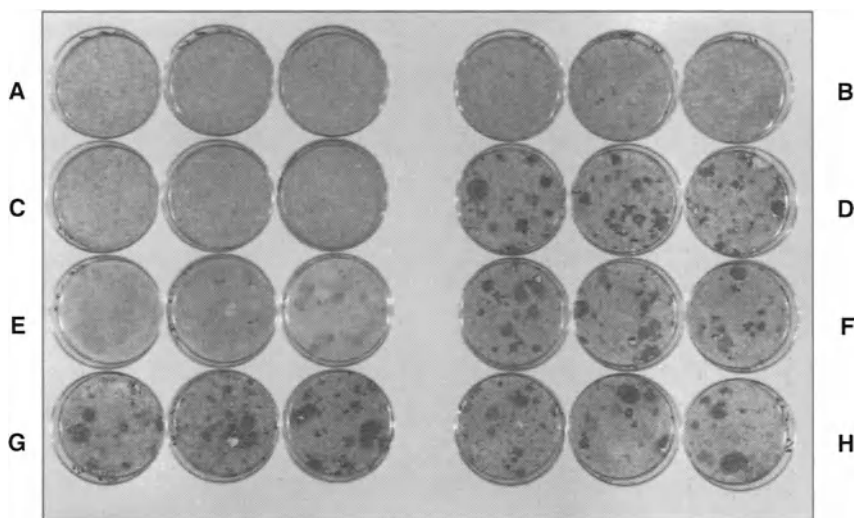


Figure 10.9 Effect of Bu_2SnCl_2 on two-stage *in vitro* transformation of BALB/c 3T3 cells. The cells (1×10^4) were initiated with MCA ($0.1 \mu\text{g ml}^{-1}$) and promoted with TPA ($0.1 \mu\text{g ml}^{-1}$). Bu_2SnCl_2 was added simultaneously with either MCA or TPA. A: whole negative controls, B: MCA alone (promotion blank), C: TPA alone (initiation blank), D: MCA-TPA (positive controls), E: $[\text{MCA} + \text{Bu}_2\text{Sn} (3 \times 10^{-7} \text{ M})]$ -TPA, F: $\text{MCA}-[\text{TPA} + \text{Bu}_2\text{Sn} (3 \times 10^{-7} \text{ M})]$, G: $[\text{MCA} + \text{Bu}_2\text{Sn} (3 \times 10^{-8} \text{ M})]$ -TPA, H: $\text{MCA}-[\text{TPA} + \text{Bu}_2\text{Sn} (3 \times 10^{-8} \text{ M})]$.

vitro results is unknown. Clearly, additional *in vivo* and *in vitro* studies on its effects are needed.

Furthermore, thymic lymphosarcoma cells (BW5147) and HeLa cells were selected as malignant culture cells, and the effects of organotin compounds on the proliferation of these cells *in vitro* were examined in comparison with those of thymocytes in which DNA synthesis is more active than in other normal tissue cells (Figure 10.10). It was found that DNA syntheses of thymic lymphosarcoma cells and HeLa cells were more dramatically inhibited, and also in a dose-related fashion, by Bu_2SnCl_2 at a concentration of more than 10^{-7} M , compared with those of mitogen and non-stimulated thymocytes. Incidentally, at concentrations between 10^{-7} M and 10^{-6} M , Bu_2SnCl_2 affected the cell viability of thymocytes only slightly, and much less that of other tissue cells. Taken together, these results suggest that Bu_2SnCl_2 may inhibit the further growth of the malignant cell population by preventing the mitotic division of the cells and that the compound may be available as an anticancer agent [28–30, 40, 92, 96, 100].

In order to make the best use of the antiproliferative activity of tin as described above, a wide variety of tin compounds have been synthesized and tested as possible anticancer agents, simulating the basic structure, such as octahedral diorganotin dihalide complexes. Table 10.6 shows the number of

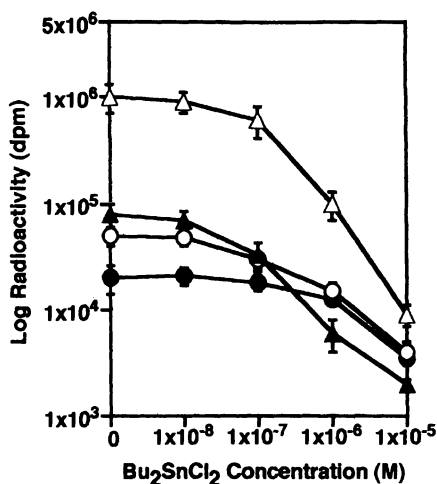


Figure 10.10 Effect of Bu_2SnCl_2 on DNA synthesis of proliferating cells. Cells (each, 1×10^6 cells ml^{-1}) were cultured with varying amounts of Bu_2SnCl_2 in octuplicate during 24 h and ^3H -thymidine was present during the last 4 h of the culture period. Vertical bars denote the SE of the mean for ten determinations. (○) Con A-stimulated thymocytes, (●) non-stimulated thymocytes, (△) thymic lymphosarcoma cells, (▲) HeLa cells.

Table 10.6 Metal and metalloid compounds tested by the National Cancer Institute

										IIIA Al 90	IVA	VA	VIA
Sc 8	Ti 87	V 84	Cr 253	Mn 273	Fe 883	Co 844	Ni 734	Cu 1275	Zn 861	Ga 59	Ge 226	As 1254	Se 734
Y 10	Zr 59	Nb 28	Mo 170	Tc 0	Ru 145	Rh 257	Pd 435	Ag 145	Cd 124	In 18	Sn 2008	Sb 353	Te 51
La ⁺ 27	Hf 15	Ta 15	W 118	Re 41	Os 25	Ir 41	Pt 1538	Au 121	Hg 823	Tl 37	Pb 288	Bi 81	Po 0
Ce 30	Pr 23	Nd 27	Pm 0	Sm 20	Eu 79	Gd 18	Tb 40	Dy 22	Ho 12	Er 18	Tm 12	Yb 13	Lu 11

metal and metalloid compounds tested by the National Cancer Institute (NCI) [107]. Among the compounds tested, the most numerous are tin (2008) with platinum (1538) next in descending order.

10.3.5 Anti-inflammatory action

Organotin compounds such as dibutyltin, tributyltin and triphenyltin significantly suppress not only the chemotactic response of neutrophils (Figure 10.11) [108–110] but also the release of arachidonic acid [108–110] and lysosomal enzymes, such as β -glucuronidase in neutrophils. Moreover, each of these suppressions is dose dependent with their dose–response curves parallel to each other [108–110]. These results focused our interest on the anti-inflammatory action of these organotin compounds since steroids such as glucocorticoids possibly exert their anti-inflammatory action by preventing the release of arachidonic acid from phospholipids, chemotaxis and the release of lysosomal enzymes.

Consequently, we assessed the anti-inflammatory action of organotin compounds on carrageenan-induced foot edema as compared with that of glucocorticoids (Figure 10.12) [111, 112]. Dibutyltin produces strong dose-dependent inhibition of the second phase, which is maintained by the release of prostaglandins, without the development of the first phase, which is maintained by histamine and serotonin. This inhibitory effect is almost the same as that of hydrocortisone, while the inhibitory effect of triorganotins is much less than that of dibutyltin. Notably, neither dibutyltin, triphenyltin nor hydrocortisone inhibit the development of the first phase of edema.

10.3.6 Tolerance manifestation against thymus atrophy

Recently we found a tolerance against dialkyltin-induced thymus atrophy and examined three possible factors for tolerance manifestation, which are

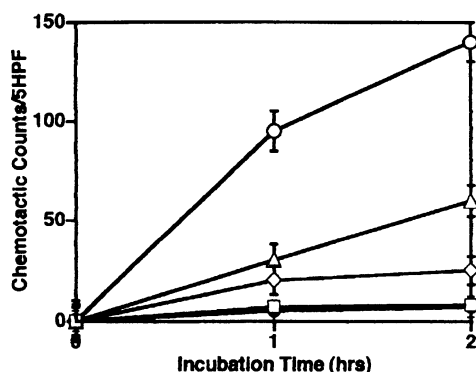


Figure 10.11 Time course of chemotactic migration of rabbit neutrophils *in vitro*. Bu_2SnCl_2 was added to the cell suspensions in the upper compartment of the Boyden chamber at the concentration of 0 (blank control, ●), 0 (positive controls, ○), 10^{-7} (Δ), 10^{-6} (◇), 10^{-5} M (□), and fMet-Leu-Phe was placed into the lower compartment of the Boyden chamber at a concentration of 10^{-8} M (positive). Each point represents the mean of five chambers. Vertical bars denote the SE of the mean for ten determinations.

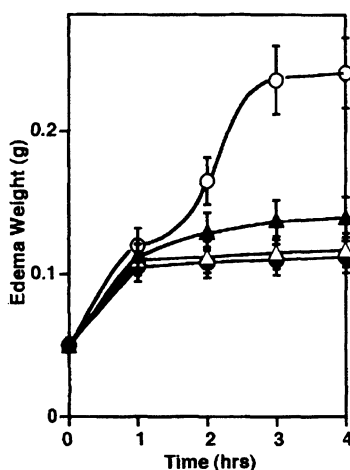


Figure 10.12 Effect of organotin compounds on the development of edema after subplantar injection of 0.5 mg of carrageenan in 0.05 ml of pyrogen-free saline. The drugs were given p.o. at a dose of 10 mg kg^{-1} 1 h before the irritant. Each point is corrected for the reading taken each time after the saline injection as blank control. Vertical bars denote the SE of the mean for eight determinations. (○) Positive controls, (●) Bu_2SnCl_2 , (▲) Ph_3SnCl , (△) hydrocortisone.

induction of (1) organotin-degrading enzyme, (2) tin-binding substances and (3) other factors blocking necrosis (or apoptosis) and toxic cell death, in order to clarify the mechanism [29, 30, 85, 93–95, 113–118].

By continuous exposure to dibutyltin, the thymus recovered from atrophy during the experimental period of 5–8 weeks (Figure 10.13). The concentration of dibutyltin in the thymus reached a maximum level after 2 weeks followed by a gradual decrease (Figure 10.14). Even during the tolerance

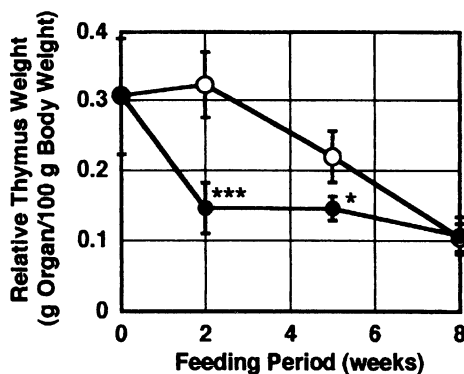


Figure 10.13 Relative thymus weight of rats fed 0 or 100 ppm Bu_2SnCl_2 throughout the experimental period. Vertical bars denote the SE of the mean for ten determinations; those marked with asterisks differ significantly (Student's *t*-test) from the corresponding control value:

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, (○) control (0 ppm) group, (●) 100 ppm group.

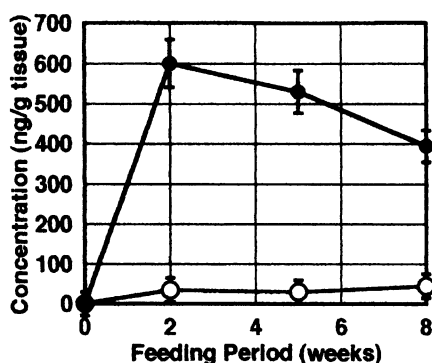


Figure 10.14 Movement of dibutyltin and its metabolites in the thymus of rats fed 100 ppm dibutyltin dichloride throughout the experimental period. Vertical bars denote the SE of the mean for ten determinations. (O) Monobutyltin, (●) dibutyltin.

manifestation, the greater part of the dibutyltin, which is at a sufficiently high level to induce thymus atrophy, was retained in its original form, i.e. in an unmetabolized form, by the thymus. The quantity of monobutyltin which was metabolized from dibutyltin was negligible compared with that of dibutyltin itself. Therefore, this tolerance is not due to inducing the generation of the degradation enzyme whose effect is the dealkylation of organotins [29, 30, 85, 113–118].

Figure 10.15 shows the distribution of organotins in various thymus extracts which are isolated as six fractions (A, B, C, D, E, F) extending from a hydrophilic fraction to a hydrophobic fraction. A large amount of organotins was found in the extract (D) of the atrophied thymus and in the extract (F) of the recovered thymus (tolerant thymus). Moreover, most of the organotins existed in the thymocytes but not in the connective tissues within the thymus.

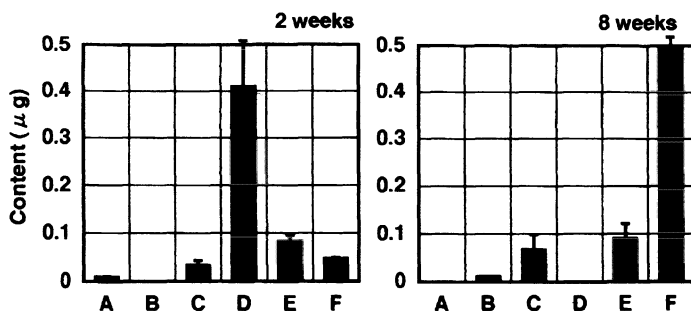


Figure 10.15 The distribution of organotins in various thymus extracts of rats fed 100 ppm dibutyltin dichloride for 2 or 8 weeks. Vertical bars denote the SE of the mean for five determinations. (A–F): thymus extracts.

These results indicate that most of the organotins are incorporated into the thymocytes but not into the connective tissues, and are transiently accumulated in the hydrophilic extract (D) (during the atrophy of the thymus) and, with continuous exposure to dibutyltin, they are then transferred to and accumulated in the hydrophobic extract (F) which consists of the insoluble fibrous tissues of the thymocytes such as membrane and tendon (during the manifestation of tolerance) [29, 30, 115-118].

Further, as shown in Figure 10.16, the continuous exposure to dibutyltin induced an increase in the concentration of zinc, that is, an increase of zinc-binding substances in the thymus extracts (A and C). In particular, as the thymus extract (A) is hydrophilic and the only fraction that contains metallothionein families, it is evident that an induction of the generation of metallothionein families is accelerated with dibutyltin exposure [29, 30, 115-118].

Therefore, the presence or induction of other factors blocking toxic cell death was investigated by observing the suppressive effects of various extracts of tolerant thymus on the dibutyltin-induced cell death of thymocytes (this is the cause of thymus atrophy). The result revealed that each of the extracts A, D and F had a significant suppressive activity against cell death as shown in Figure 10.17 [29, 30, 116-118].

From these results, this tolerance manifestation against organotin-induced thymus atrophy appears to be due to the accumulation of organotin in the hydrophobic tin-binding substance which exists in the insoluble fibrous tissues of the thymocytes like membrane and tendon, or to the induction of cell death suppression factors in the hydrophilic extract which contains metallothionein families, but not to the induction of organotin-degrading enzyme.

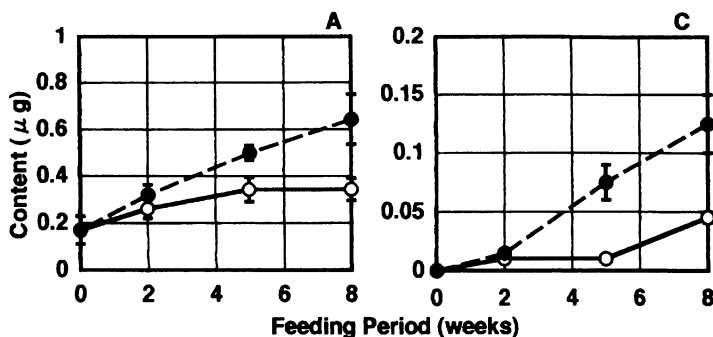


Figure 10.16 Movement of zinc in various zinc-binding thymus extracts of rats fed 0 or 100 ppm dibutyltin dichloride throughout the experimental period. Vertical bars denote the SE of the mean for five determinations. (A, C): thymus extracts, (O): control (0 ppm) group, (●): 100 ppm group.

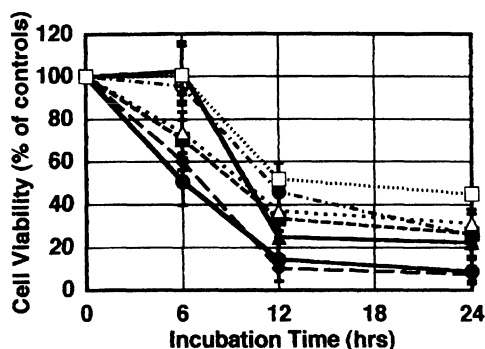


Figure 10.17 Suppression of cell death by various thymus extracts of rats fed 100 ppm dibutyltin dichloride for 8 weeks. Thymocytes ($1\text{--}5 \times 10^6$ cells ml^{-1}) were incubated with the same quantity of each thymus extract: A(▲), B(■), C(◆), D(○), E(△), F(□) in the presence (●) of 5×10^{-6} M dibutyltin dichloride at 37°C for 6, 12 and 24 h. Vertical bars denote the SE of the mean for five determinations.

10.4 Cellular and biochemical aspects of the activity manifestation

10.4.1 Intracellular distribution of organotins

The bioactivity of alkyltin derivatives depends on their solubility in biological fluids and the extent of their incorporation into the cells, i.e. their intracellular distributions, which are provided by the number and length of their organic ligands.

Therefore, the intracellular locations of organotins following their entry into the cells were initially visualized by using a fluorescent labeling technique [119]. This visualization revealed that hydrophobic organotin compounds such as dibutyl-, tributyl- and triphenyltin selectively accumulated in the Golgi apparatus and endoplasmic reticulum (ER) region but not in the nucleus (Figure 10.18) [28–30, 120–122]. This was further confirmed by using organelle-destroying agents such as monensin or nocodazole. After the destruction of the Golgi apparatus and ER by the treatment with monensin or nocodazole, hydrophobic organotin disperses throughout the cytoplasm [121]. In addition, the accumulation in the region of the Golgi apparatus and ER was inhibited when fixed cells were washed with Triton-X 100 before incubation with organotins (data not shown). These results support the idea that hydrophobic organotin compounds selectively accumulate in the region of the Golgi apparatus and ER.

It is possible that almost all organotin compounds are incorporated into the cells in vesicle form by fusion, or in a similar fashion to the incorporation of the cation form. In particular, in the transport of organotins to the Golgi apparatus and ER, cellular processes such as endocytosis are not involved because certain hydrophobic organotins accumulate in these areas in both

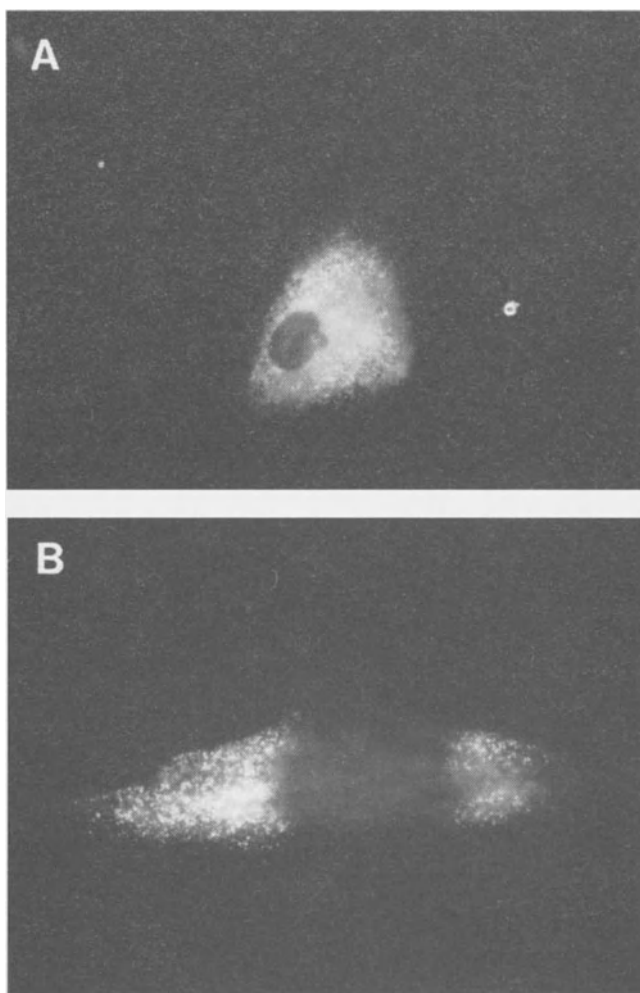


Figure 10.18 Intracellular distribution of various organotin compounds in fixed cells. Human skin fibroblasts were fixed with 0.5% glutaraldehyde for 10 min at room temperature, washed and incubated for 10 min at 37 °C with 50 μM Bu_2SnCl_2 (A) or 100 μM Me_2SnCl_2 (B). The cells were then washed, incubated with 100 $\mu\text{g ml}^{-1}$ morin for 5 min at 37 °C, washed again and photographed.

intact and fixed cells. It may be that the organotins are transported to the Golgi apparatus and ER by their hydrophobicity, that is, their liposolubility or their affinity for intracellular lipids and lipophilic proteins, because Golgi and ER labeling is inhibited by Triton-X 100 washing, as mentioned above. Within the cells, dialkyltin may exist as distannoxane, and trialkyltin may exist as bisoxide (dimer), or as many kinds of polymers in both halide form and hydroxide form [28–30, 120–122].

10.4.2 *Effects on structure and function of the Golgi apparatus and endoplasmic reticulum*

The specific stratified structure of the Golgi apparatus can be observed clearly by using fluorescent ceramide. However, the structure is completely destroyed by the presence of dibutyltin (Figure 10.19). Further, dibutyltin suppresses such Golgi functions as the lipid metabolism. In particular,

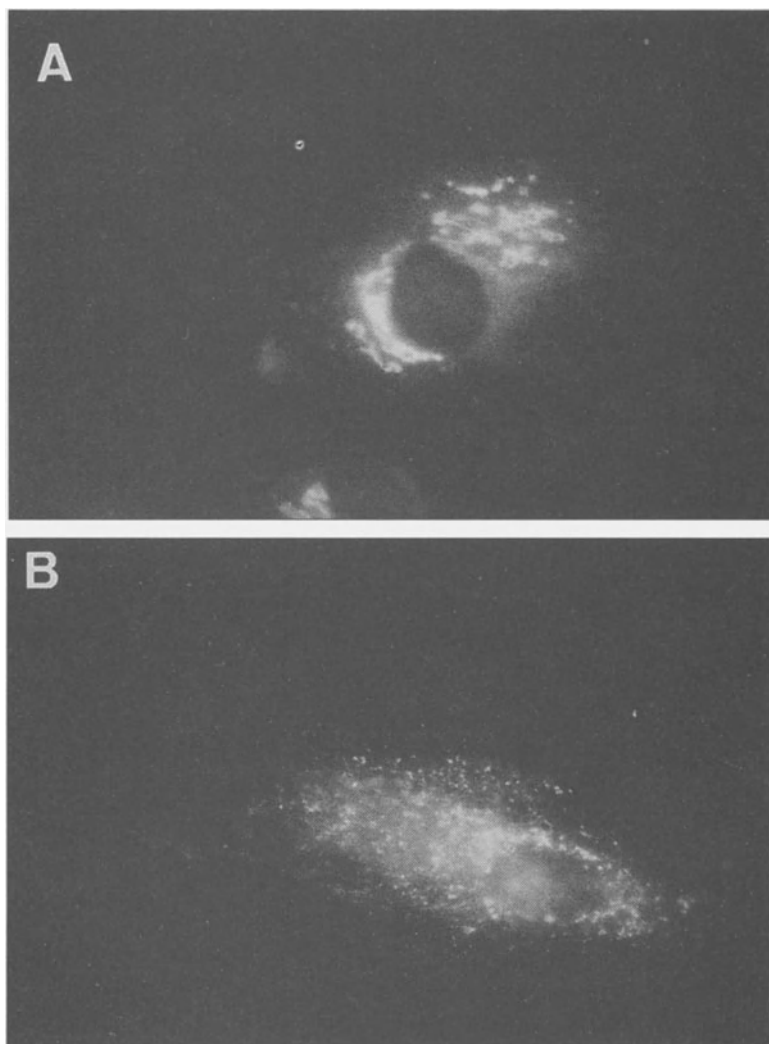


Figure 10.19 Effects of organotin compound on the morphology of the Golgi apparatus in living cells. Human skin fibroblasts (SF-TY) were incubated in the absence (A) or presence (B) of $1\text{ }\mu\text{M}$ Bu_2SnCl_2 for 2 h and were then stained with $\text{C}_6\text{-NBD-ceramide-BSA}$ and viewed in the fluorescence microscope.

ceramide metabolism to glucosylceramide and sphingomyelin is significantly impaired (Figure 10.20). These results illustrate that the suppression of Golgi functions by organotins may be due to the destruction of the Golgi apparatus structure [28–30, 120, 121, 123, 124].

Similarly, tributyltin and dibutyltin selectively destroy the characteristic reticular structure of the ER (Figure 10.21). The ER network is retracted from the periphery and large cisternae are formed [28–30, 123, 125]. Furthermore, these hydrophobic organotins inhibit such ER functions as inositol 1,4,5-triphosphate (IP_3)-induced intracellular Ca^{2+} mobilization by promoting Ca^{2+} release in a similar fashion to IP_3 (Figure 10.22) [121, 126]. This inhibition appears to be due to the alteration or the destruction of the ER membrane structure. Monobutyltin and tetrabutyltin do not affect either the structure or the function of the ER [121, 123, 125, 126].

From the results observed in the Golgi apparatus and the ER, the action of organotin compounds on each organelle appears to depend primarily on their intracellular distribution, which is generated by their lipotropy, specifically the number and length of their organic ligands.

10.4.3 Effects of phospholipid membrane on physical properties

The activation of phospholipid transport between organelles is known to be affected by the physical properties of the membrane [127, 128]. In particular, phospholipids of the Golgi apparatus and the ER are considered to be transported to the plasma membrane in vesicle form by vesicle budding and fusion, as shown in Figure 10.23.

Dibutyltin also affects the membrane order of various phospholipid vesi-

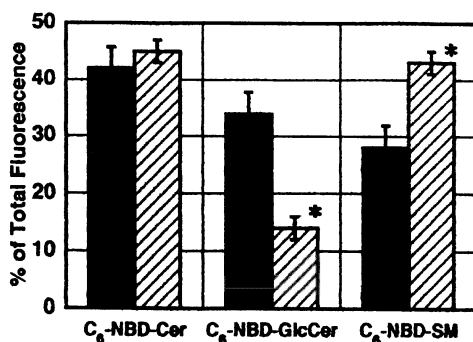


Figure 10.20 Effects of organotin compound on the metabolism of C_6 -NBD-ceramide in Golgi apparatus. CHO cells were incubated without (controls, ■) and with $10\ \mu\text{M}$ Bu_3SnCl_3 (▨) for 3 h and then incubated with C_6 -NBD-Cer/BSA. Each value represents the mean \pm SE of four independent experiments; those marked with asterisks differ significantly (Student's t -test) from the corresponding control value (* $p < 0.001$). Cer: ceramide, GlcCer: glucosylceramide, SM: sphingomyelin.

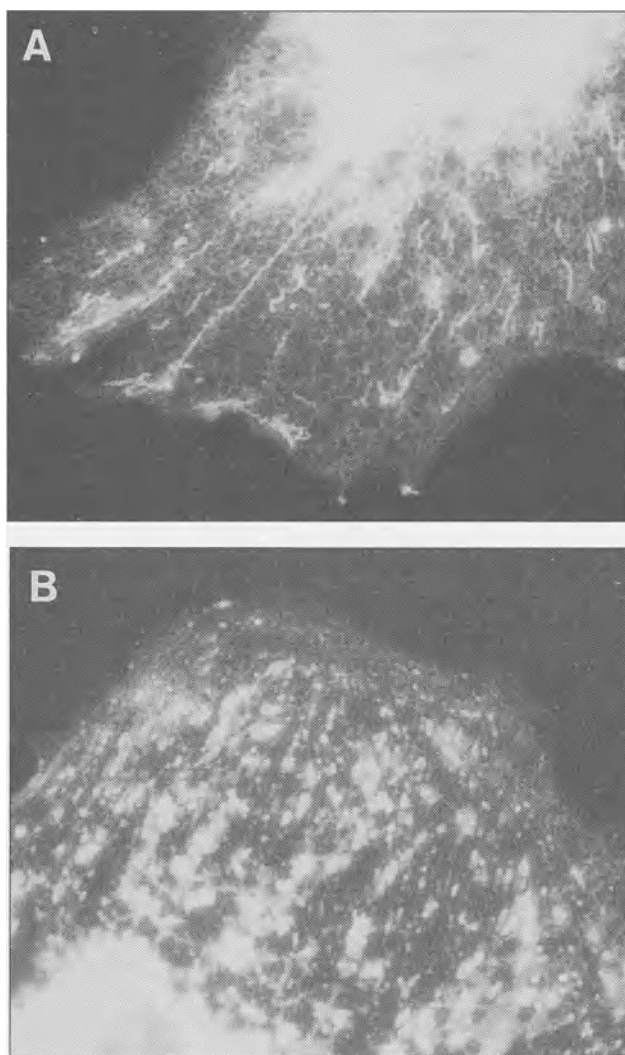


Figure 10.21 Effects of organotin compounds on the morphology of the endoplasmic reticulum (ER) in living cells. African green monkey kidney epithelial cell line (CV-1) was incubated in the absence (A) or presence (B) of $5\text{ }\mu\text{M}$ Bu_3SnCl for 10 min at 37°C . Further, the cells were fixed with 0.5% glutaraldehyde for 5 min at room temperature, washed and incubated with $2.5\text{ }\mu\text{g ml}^{-1}$ $\text{DiOC}_6(3)$ (3,3'-dihexyloxacarbocyanine iodide) for 15 s at room temperature. The cells were then washed and photographed.

cles (Figure 10.24) [127,129]. In particular, dibutyltin shows a far stronger 'ordering' effect on phosphatidylinositol 4-monophosphate (PIP_1) and phosphatidylinositol 4,5-diphosphate (PIP_2) vesicle membranes than on other phospholipid vesicle membranes. These effects are dose dependent. This

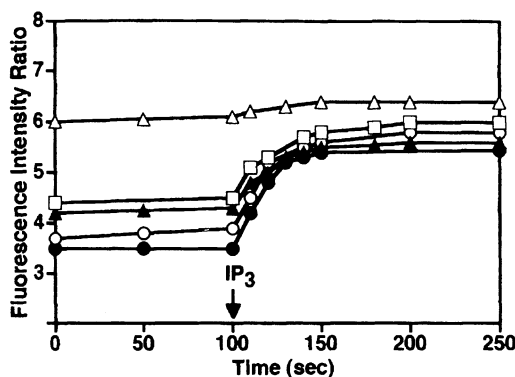


Figure 10.22 Effects of organotin compounds on Ins (1,4,5) P_3 -induced intracellular Ca^{2+} mobilization. Saponin-permeabilized RBL-2H3 cells (5×10^6 cells ml^{-1}) were incubated with 5×10^{-6} M individual organotin compound for 10 min after the addition of $1.5 \mu M$ Fura-2. The kinetics of Ca^{2+} release were resolved by determination of fluorescence intensity ratio using the dual excitation mode of 335 and 375 nm following the addition of 333 nM IP_3 . Each point denotes the mean for five determinations. (O) Controls, (●) $BuSnCl_3$, (Δ) Bu_3SnCl , (\blacktriangle) Bu_4Sn , (\square) TBTO.

finding appears to provide clues to the inhibitory mechanism of dibutyltin on PI turnover, as noted below. The reason for this is that PIP_2 is the immediate target in provoking the breakdown of inositol phospholipid. PIP_2 is the substrate which is hydrolyzed to diacylglycerol [130–132] and inositol phosphate or inositol polyphosphate [133–135] by phospholipase C.

10.4.4 *Suppressive effects on the cell proliferation system*

Proliferating cells such as thymic lymphocytes were more sensitive to dialkyltin compounds such as dibutyltin and dioctyltin than to other organotin compounds, and also more sensitive than tissue cells of other organs (Table 10.7).

As was shown in Figure 10.6, DNA synthesis of the thymic lymphocytes was significantly inhibited by dibutyltin even at the concentration of 10^{-7} M at which cell viability was not yet impaired. Moreover, a parallel between dose-response curves of dibutyltin for DNA synthesis and cell viability was observed. These results indicate that dibutyltin primarily induces an inhibition of cell proliferation and secondly causes cell death [28–30, 92, 128, 136–139].

At present, the mechanism of cell proliferation and transformation is not fully understood. However, some hypotheses are proposed for the main pathway leading to DNA synthesis and ultimate mitotic division [140–164]. In either case a signal transduction leading to DNA synthesis appears to be initiated by stimulating the phospholipase activation system and provoking

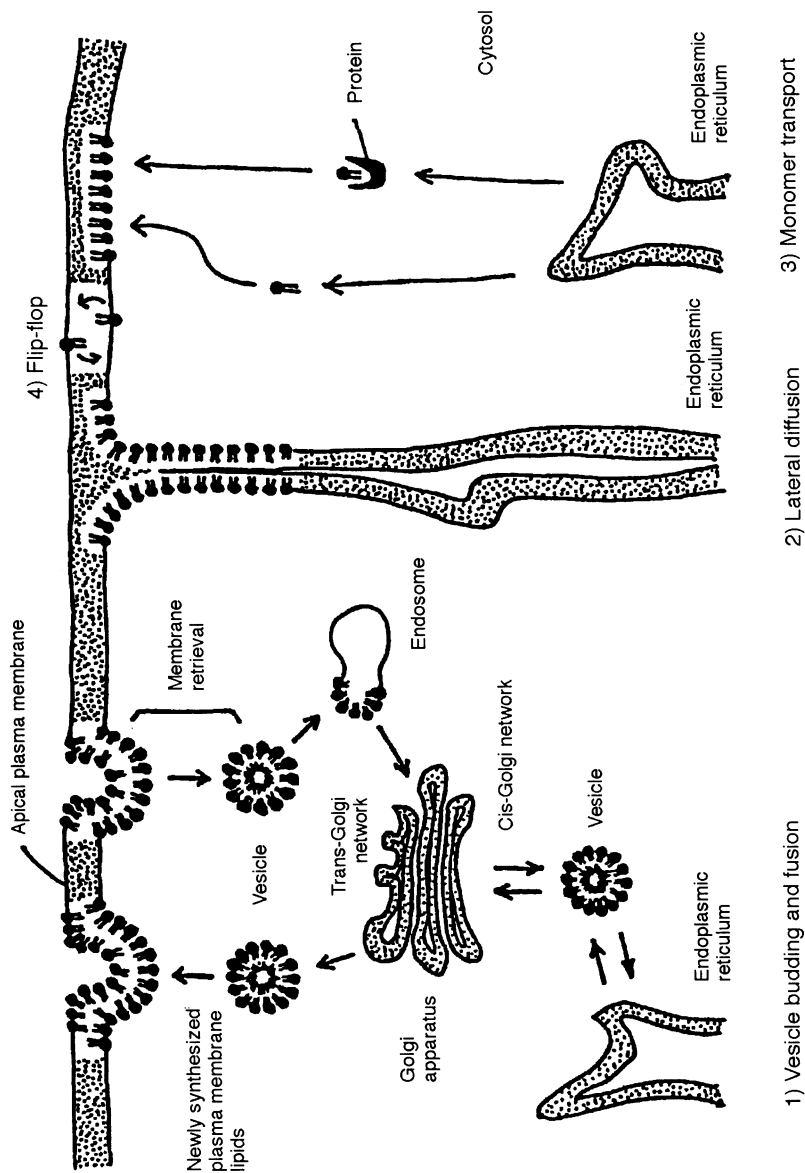


Figure 10.23 The proposed intracellular transport of phospholipids.

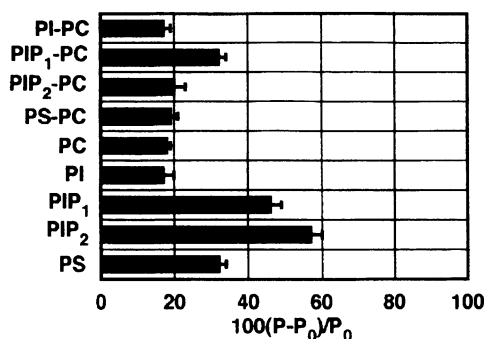


Figure 10.24 Effect of Bu_2SnCl_2 on the membrane order of various phospholipid vesicles. Each phospholipid vesicle containing DPH in 20 mM Tris-HCl buffer (pH 7.5, containing 100 mM NaCl) was incubated without and with Bu_2SnCl_2 (10^{-4} M) for 5–7 min at 25°C and the membrane order was measured by fluorescence polarization. Each value was expressed as a percentage change in the degree of fluorescence polarization, $100(\text{P}-\text{P}_0)/\text{P}_0$. All the phospholipid vesicles contained $18 \mu\text{g ml}^{-1}$ total phospholipid. In the case of the mixture vesicles, the ratio of each phospholipid to PC is $1/2$. Horizontal bars denote the SE of the mean for ten determinations.

Table 10.7 Inhibition of thymidine uptake in rat lymphoid cells and tissue cells by dibutyltin compound

Molarity of Bu_2SnCl_2	Uptake of ^3H -labeled thymidine (% of controls)				
	Thymocytes	Spleen cells	Liver cells	Kidney cells	Brain cells
1×10^{-4} M	15.8 ± 0.3	16.8 ± 0.4	61.1 ± 1.7	62.1 ± 1.0	95.4 ± 2.8
1×10^{-6} M	26.0 ± 0.5	33.7 ± 0.7	89.5 ± 2.5	92.1 ± 2.7	106.2 ± 3.1

Cells (10^6 cells ml^{-1}) of each organ were cultured with or without Bu_2SnCl_2 during 24 h, and [^3H]-thymidine was present during the last 4 h of the culture period. Each value is expressed as a percentage of the control value obtained in the absence of Bu_2SnCl_2 , and is the mean \pm SE of 10 determinations.

phosphatidylinositol (PI) turnover and arachidonate release (Figure 10.25). Therefore, the inhibition mechanism of dibutyltin on the cell proliferation was examined using the lymphocyte transformation which has been most fully defined as a model [28–30, 37, 92, 97, 99, 100, 108, 111, 112, 165, 166, 167].

Of the many results tested, that is, of the early events leading to DNA synthesis, RNA synthesis was seen to be significantly inhibited by dibutyltin concentrations exceeding 10^{-7} M (Figure 10.26). However, Ca^{2+} entry into the cells, which may be one of the main pathways leading to DNA synthesis, was not inhibited at all by dibutyltin (Figure 10.27). The effect of dibutyltin on phospholipid synthesis is portrayed in Figure 10.28. Total phospholipid synthesis was significantly inhibited by dibutyltin of more than 10^{-7} M [28–30, 92, 96, 101, 128]. Thus, further examination was carried out as to whether or not this inhibition was restricted to certain phosphatides.

As shown in Figure 10.29, the most remarkable change observed at the

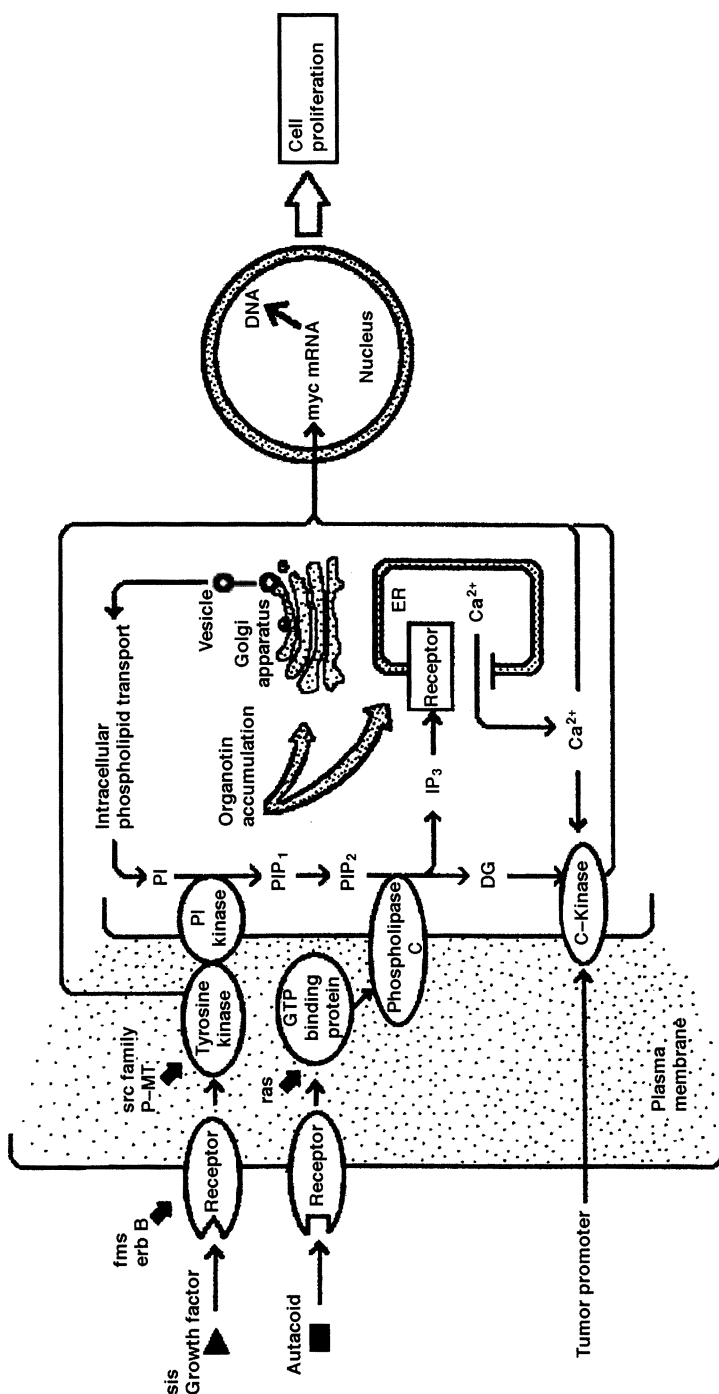


Figure 10.25 Some hypotheses proposed for a main pathway leading to cell growth and transformation.

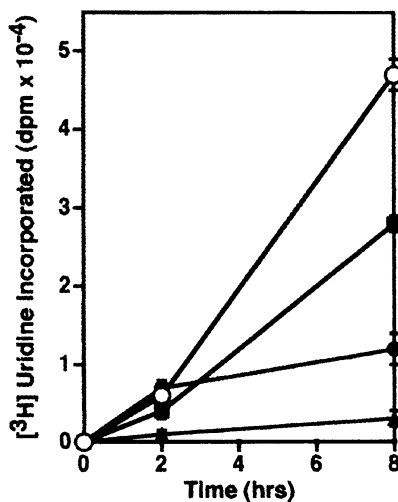


Figure 10.26 Effect of organotin compounds on RNA synthesis. Incorporation of $[^3\text{H}]$ -uridine into RNA of thymocytes (10^6 cells ml^{-1}) after stimulation with Con A ($5 \mu\text{g ml}^{-1}$) was measured in the absence (O) and presence of 10^{-7} M Bu_3SnCl_2 (▲), 10^{-7} M Ph_3SnCl (●), or 10^{-7} M MeSnCl_3 (■). Each point is corrected for radioactivity incorporated without Con A at each incubation time.

Vertical bars denote the SE of the mean for five determinations.

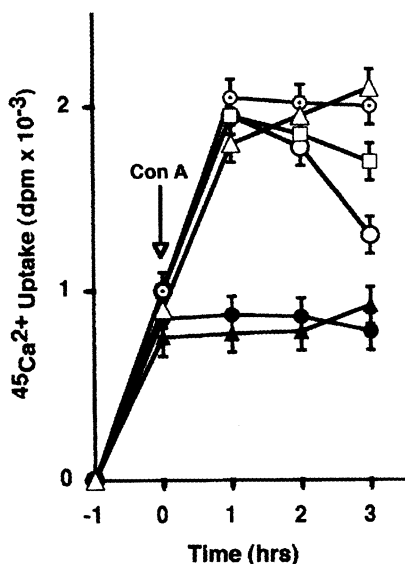


Figure 10.27 Effect of organotin compounds on calcium uptake. Incorporation of $^{45}\text{Ca}^{2+}$ into thymocytes (10^6 cells ml^{-1}) after stimulation with Con A ($5 \mu\text{g ml}^{-1}$) was measured in the absence (O) and presence of 10^{-7} M Bu_3SnCl_2 (▲), 10^{-7} M Ph_3SnCl (●), or 10^{-7} M MeSnCl_3 (■), and $^{45}\text{Ca}^{2+}$ uptake by non-stimulated thymocytes was measured in the absence (●) and presence (▲) of 10^{-7} M Bu_3SnCl_2 . Vertical bars denote the SE of the mean for five determinations.

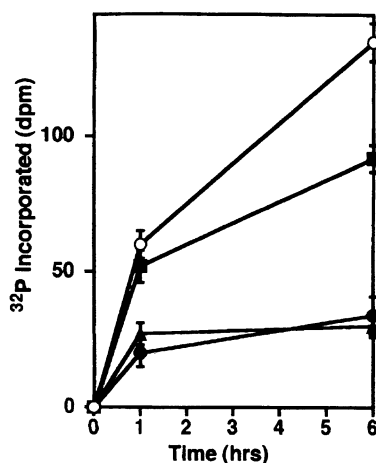


Figure 10.28 Effect of organotin compounds on phospholipid synthesis of rat thymocytes. Phospholipid synthesis was measured by the incorporation of ^{32}P into the lipid fraction of the cultured cells (1.5×10^6 cells ml^{-1}) after stimulation with Con A ($5 \mu\text{g ml}^{-1}$) in the absence (○) and presence of 10^{-7} M Bu_2SnCl_2 (●), 10^{-7} M MeSnCl_3 (■), or 10^{-7} M Ph_3SnCl (▲). Each point is corrected for radioactivity incorporated without Con A at each incubation time. Vertical bars denote the SE of the mean for five determinations.

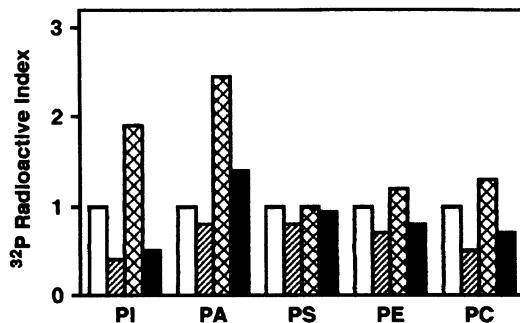


Figure 10.29 Effect of Bu_2SnCl_2 on phospholipid metabolism. Rat thymocytes (3×10^6 cells ml^{-1}) prelabeled with ^{32}P -phosphoric acid ($10 \mu\text{Ci ml}^{-1}$) were treated without and with Con A ($5 \mu\text{g ml}^{-1}$) in the absence and presence of Bu_2SnCl_2 (5×10^{-7} M) for 5 min. The mean radioactivity of each phospholipid component separated from the control culture (□) was taken as 1.0 and was compared to that of the corresponding phospholipid component from the experimental cultures treated with Bu_2SnCl_2 (▨), Con A (▩) and Con A plus Bu_2SnCl_2 (■).

earliest stage of lymphocyte transformation is increases in PI and phosphatidic acid (PA) synthesis, namely the acceleration of PI turnover [150, 152]. However, the presence of dibutyltin of more than 10^{-7} M inhibited this remarkable acceleration. Moreover, a parallel was found between the dose-dependent inhibition of acceleration of PI turnover and that of DNA synthesis by dibutyltin. Increases in phosphatidylserine (PS), phosphatidyl-

ethanolamine (PE) and phosphatidylcholine (PC) synthesis were not observed during the first 5–30 min of the lymphocyte stimulation, and exposure of at least 2–3 h was required for significant increases [28–30, 92, 128].

On the other hand, the degradation of phospholipids was also inhibited by the presence of dibutyltin. Figure 10.30 shows the variation with time of arachidonate release from phospholipids by phospholipase A_2 . The acceleration of arachidonate release was significantly inhibited by dibutyltin of more than 10^{-7} M. However, no direct inhibitory effects of organotin compounds on phospholipase A_2 , C and D were found, although the substrate was hydrolyzed to three main products depending upon the species of phospholipase (Table 10.8) [108, 111, 128, 168].

10.4.5 Excessive accumulation of olfactory calcium and inhibition of olfactory signal transduction

Recently, we found that tributyltin produced extensive necrosis and cell loss in the areas of the olfactory cortex and pyriform cortex (Figure 10.2), and that the compound selectively induced an excessive accumulation of calcium in the olfactory bulb (Figure 10.31) [53–55]. Collectively, these results support the hypothesis that the excessive accumulation of calcium plays a significant role in cell necrosis (or apoptosis) and may contribute to toxic cell death caused by tributyltin. The mechanism of excessive accumulation of calcium into the olfactory bulb was therefore examined kinetically by using a single intraperitoneal administration of tributyltin.

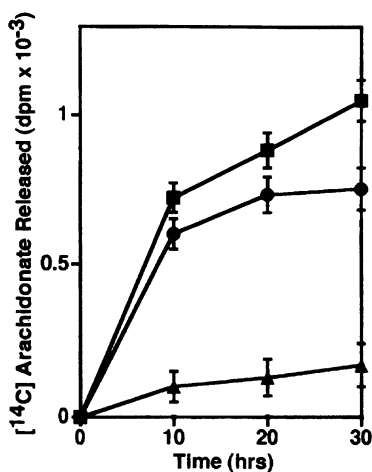


Figure 10.30 Time course of release of arachidonic acid. [^{14}C]-Arachidonate release was measured after stimulation with $5\text{ }\mu\text{g}$ of Con A in the absence (●) and presence of 10^{-7} M Bu_3SnCl_2 (▲) or 10^{-7} M MeSnCl_3 (■). Each point is corrected for radioactivity released without Con A at each incubation time. Vertical bars denote the SE of the mean for five determinations.

Table 10.8 *In vitro* effect of organotins on various phospholipase activities

Enzyme source	Spot no.	Phosphatidylcholine hydrolyzed (% of total counts)			
		Control	Organotin added ($1 \times 10^{-7}M$)		
			Bu_2SnCl_2	Bu_3SnCl	Ph_3SnCl
Phospholipase A ₂ (porcine pancreas)	1	25.0±0.7	27.3±0.2	31.3±0.8	30.1±0.7
	2	5.5±0.2	7.3±0.3	8.2±0.9	9.0±1.2
	3	4.8±0.1	5.9±0.5	7.1±1.1	6.5±0.7
Phospholipase C (<i>B. cereus</i>)	1	7.5±1.3	8.2±1.0	5.3±0.5	6.8±0.3
	2	0.7±0.2	0.7±0.1	0.6±0.1	1.0±0.2
	3	70.0±4.2	63.0±2.8	75.0±5.9	63.0±3.1
Phospholipase D (cabbage)	1	15.8±0.9	17.4±1.2	17.6±1.2	16.8±0.7
	2	1.0±0.1	1.3±0.1	1.4±0.1	0.9±0.1
	3	1.5±0.3	2.3±0.2	2.1±0.2	1.4±0.1

The spot numbers indicated the hydrolyzed components of substrate, L- α -dipalmitoyl-[choline-methyl- ^{14}C]-phosphatidylcholine. The total recovered radioactivity from one sample was taken as 100% and the relative radioactivity in each spot was determined from this value. Each value is the mean \pm SE of five determinations.

Tributyltin was quickly distributed to the olfactory bulb and the concentration of tributyltin reached a maximum within a day, decreasing rapidly during the subsequent 3 days (Figure 10.31) [53–55]. Under this tributyltin exposure condition, the concentration of calcium in the olfactory increased slowly during the first day and then rose steeply to extremely high levels after 2 days, followed by a rapid decrease in a similar pattern (Figure 10.31) [53–55].

A parathyroid hormone (PTH), which regulates the concentration and distribution of such mineral ions as Ca^{2+} and Mg^{2+} , selectively and significantly increased only in the olfactory bulb, in spite of the fact that there was

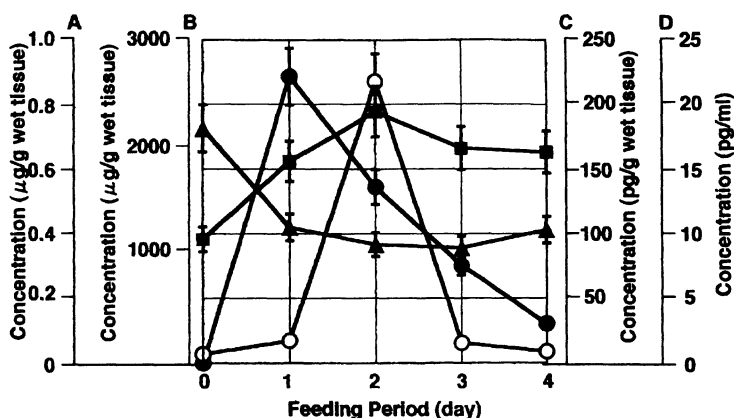


Figure 10.31 Movement of organotin, calcium and parathyroid hormone (PTH) in the olfactory and the serum of rats given a single intraperitoneal injection of tributyltin chloride (2.0 mg kg^{-1} body weight). Vertical bars denote the SE of the mean for five determinations. Organotin in the olfactory (● in the A axis), calcium in the olfactory (○ in the B axis), PTH in the olfactory (■ in the C axis), PTH in the serum (▲ in the D axis).

no change in PTH level of other brain tissues, and reached a maximum level after 2 days, followed by a gradual decrease (Figure 10.31) [53–55]. In this connection, the serum PTH level decreased in contrast to the pattern of increasing olfactory PTH. This decrease seems to be a compensatory suppression to reduce high Ca^{2+} levels in the tissues. Therefore, tributyltin seems to induce selectively an excessive increase of olfactory calcium by mediating PTH function.

Inositol-1,4,5-triphosphate (IP_3) rapidly decreased with time and reached a minimum level (about 50% of the control) after 3 days (Figure 10.32) [57–59]. IP_3 appears to serve as an intracellular second messenger to mediate odorant transduction by stimulating the IP_3 -gated Ca^{2+} channel that could mediate the Ca^{2+} influx, leading to a rapid increase of intracellular Ca^{2+} [169, 170], as well as in the case of an IP_3 -induced intracellular Ca^{2+} mobilization in the endoplasmic reticulum (ER) (section 10.4.2). Therefore, it does not appear, in the case of tributyltin exposure, that Ca^{2+} influx through a plasma membrane IP_3 -gated Ca^{2+} channel and Ca^{2+} release through an IP_3 receptor channel complex from ER contribute to a rapid and excessive increase of intracellular Ca^{2+} .

Cyclic adenosine monophosphate (cAMP) rapidly increased and reached a maximum within a day and the maximum level was maintained for 2 days followed by a rapid decrease (Figure 10.32) [57–59]. cAMP, the level of which is regulated by intracellular Ca^{2+} [171], is formed by Ca^{2+} -activated adenylyl

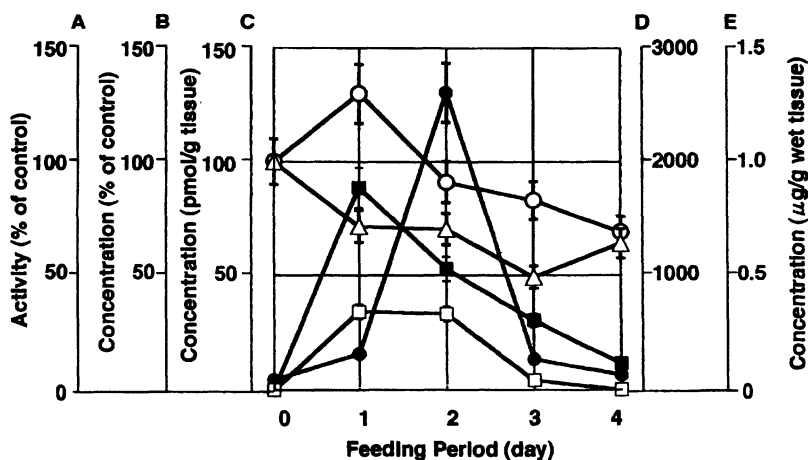


Figure 10.32 Changes with the passage of time in the activity of Ca^{2+} /calmodulin-dependent protein kinase II (○ in the A axis), in the concentration of inositol-1,4,5-triphosphate (IP_3) (△ in the B axis), cAMP (□ in the C axis), calcium (● in the D axis) and organotin (■ in the E axis) in the olfactory of rats given a single intraperitoneal injection of tributyltin chloride (2.0 mg kg^{-1} body weight). Each cAMP value in the C axis is corrected for the value taken without tributyltin at each feeding period. Vertical bars denote the SE of the mean for five determinations.

cyclase [172, 173] and appears to serve as an intracellular second messenger in the olfactory signal transduction by stimulating a cAMP-activated channel that would allow the influx of extracellular Ca^{2+} as well as a plasma membrane IP_3 -gated channel [174]. Therefore, tributyltin appears to accelerate Ca^{2+} influx through the cAMP-activated channel by producing an excessive increase of cAMP mediated by activation of adenylyl cyclase.

Further, the activity of calcium/calmodulin-dependent protein kinase II (CaM kinase II) showed a transient increase after a day followed by a rapid and significant decrease during the subsequent 3 days (Figure 10.32) [57–59]. CaM kinase II is one of the Ca^{2+} -binding proteins and one of the protein phosphorylating enzymes that phosphorylates components of the olfactory signal transduction pathway. Moreover, the enzyme contributes to the termination process of second messenger signaling in olfaction [175] and would regulate Ca^{2+} -endonuclease fragmentation of DNA that contributes to necrosis *in vivo* or toxic cell death *in vitro* [176, 177]. Therefore, tributyltin seems to induce a loss of CaM kinase II activity by producing a rapid and excessive increase of olfactory calcium and subsequently causing DNA fragmentation and toxic cell death by the loss of the enzyme activity, although the activity of the enzyme transiently rises when olfactory calcium reaches to the concentration suitable for activation.

Putting all these results together, a trialkyltin-induced excessive increase of calcium in the olfactory bulb is associated with an increase of olfactory PTH. Since the IP_3 level in the olfactory bulb decreases significantly under the tributyltin exposure, which seems to be a consequence of tributyltin-induced inhibition of PI turnover as portrayed in Figure 10.29, the excessive increase of olfactory calcium is not due to an influx of Ca^{2+} mediated by a plasma membrane IP_3 -gated Ca^{2+} channel and a release of intracellular Ca^{2+} mediated by the IP_3 receptor-channel complex from endoplasmic reticulum (ER) (section 10.4.2). The tributyltin-induced excessive increase of olfactory calcium is perhaps caused by an excessive increase in the formation of cAMP mediated by activation of adenylyl cyclase and an excessive influx of extracellular Ca^{2+} mediated by cAMP-activated channels. Moreover, this rapid and excessive increase in the concentration of intracellular Ca^{2+} seems to put out of order CaM kinase II functions leading to necrosis *in vivo* or toxic cell death *in vitro* (Figure 10.33).

10.4.6 Discussion

Taking the cell biochemical results into consideration with the cell biological results, we propose that the biological action of organotin compounds appears to be due to several processes:

- their incorporation into the cells in vesicle form by fusion or in a similar fashion to their incorporation in cationic form;

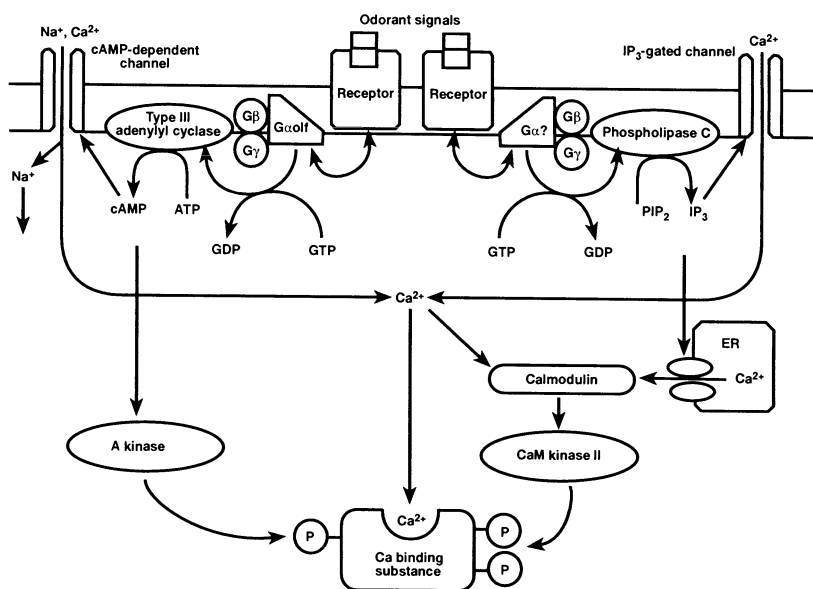


Figure 10.33 A scheme of the mechanism proposed for olfactory signal transduction.

- transport to and accumulation in the region of Golgi apparatus and ER but not to or in the plasma membrane and nucleus because of their hydrophobicity;
- the inhibition of intracellular phospholipid transport between organelles through an impairing of the structure and functions of the Golgi apparatus and the ER;
- inhibition of the membrane-mediated signal transduction system leading to DNA synthesis via phospholipid turnover and Ca^{2+} mobilization in the cell proliferation systems [28–30, 85, 92, 128, 167] or the disorder of the membrane-mediated Ca^{2+} homeostasis via various channel functions on the plasma and organelle membranes and protein phosphorylation in the olfactory signal transduction systems [53–59].

10.5 Conclusion

Tin generates a wide variety of biological activities deriving from its chemical character. In this article, the biological activities of tin compounds are discussed with a focus on the connection with immunity and the nervous system on the basis of our data. Some tin compounds are being gradually but surely eliminated as environmental contaminants, while others are expected to be developed as new medicines. In the future, tin studies may be able to

contribute valuable suggestions in the areas of thymic immunity and immune supervisory control, and in carcinogenesis and aging. Recently, originating from the tin studies noted throughout, a number of international conferences and international symposia are now being held with greater regularity, with the subsequent interest in tin compounds becoming increasingly more internationally aroused.

Abbreviations

ATP	adenosine 5'-triphosphate	<i>N</i>	number of animals
BSA	bovine serum albumin	NBD	4-nitrobenzo-2-oxal-1,3-diazole
Bu	butyl	Oc	octyl
BuSnCl ₃	monobutyltin trichloride	Oc ₂ SnCl ₂	dioctyltin dichloride
Bu ₂ SnCl ₂	dibutyltin dichloride	<i>p</i>	significant difference
Bu ₃ SnCl	tributyltin chloride	P	fluorescence polarization
Bu ₄ Sn	tetrabutyltin	PA	L- α -phosphatidic acid
BW	body weight	PC	L- α -phosphatidylcholine
CaM kinase II	Ca ²⁺ /calmodulin-dependent protein kinase II	PE	L- α -phosphatidylethanolamine
cAMP	cyclic adenosine monophosphate	Ph	phenyl
Cer	ceramide	Ph ₃ SnCl	triphenyltin chloride
CHO	Chinese hamster ovary	PHA	phytohemagglutinin
Con A	concanavalin A	PI	L- α -phosphatidylinositol
DAG	diacylglycerol	PIP ₁	L- α -phosphatidylinositol 4-mono-phosphate
DMBA	7,12-dimethylbenzanthracene	PIP ₂	L- α -phosphatidylinositol 4,5-diphosphate
DNA	deoxyribonucleic acid	Pr	propyl
DPH	1,6-diphenyl-1,3,5-hexatriene	Pr ₂ SnCl ₂	dipropyltin dichloride
ER	endoplasmic reticulum	PS	L- α -phosphatidylserine
fMet-Leu-Phe	<i>N</i> -formyl-methionylleucylphenylalanine	PTH	parathyroid hormone
GlcCer	glucosylceramide	PVC	polyvinylchloride
³ H	tritiated	RBL	rat basophilic leukemia
IP ₃	inositol 1,4,5-triphosphate	RNA	ribonucleic acid
LTP	long term potentiation	SE	standard error
MCA	20-methylcholanthrene	SM	sphingomyelin
Me	methyl	TBTO	bis(tributyltin) oxide
MeSnCl ₃	monomethyltin trichloride	T/C	the ratio of survival time of treated animals to that of control animals
Me ₂ SnCl ₂	dimethyltin dichloride	TPA	12- <i>o</i> -tetradecanoylphorbol-13-acetate

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11 Health and safety aspects of tin chemicals

PETER J. SMITH

11.1 Introduction

World consumption of tin metal in 1993 was 225 000 tonnes [1]. Tin chemicals have significantly increased their share of this figure, from an estimated 6% in the 1970s to around 15% in 1992–1993. This is expected to continue to grow, due to their wide range of industrial applications (Chapter 12) and, in many instances, to their generally low toxicity. Some health and safety problems have arisen, however, with certain of the biologically active trialkyltin compounds, which have resulted in restrictions being placed on their use in specific areas. These are discussed in section 11.3.

Tin is a non-toxic metal [2] and is reported to be an essential trace element [3, 4]. Experimental evidence is available to support the latter suggestion [5, 6] but this has not yet been universally accepted and more work is required in the area [2]. Metallic tin is non-toxic when administered orally to rats (acute oral $LD_{50} > 2000 \text{ mg kg}^{-1}$ [R.R. Dean, personal communication]) or to birds [7–9]. Tin is replacing toxic heavy metals, e.g. lead, in applications such as lead-free solders and tin foil wine bottle capsules [1].

Publications are available on the health and safety aspects of inorganic tin [10–12] and organotin [10–15] derivatives and safety data sheets on many of these compounds may be obtained from the primary (section 11.4) and speciality [16, 17] chemical manufacturers.

11.2 Inorganic tin compounds

Inorganic tin compounds have a low toxicity, as illustrated by their acute oral LD_{50} values in rats (Table 11.1), which are mostly in excess of 2000 mg kg^{-1} . For the two tin(II) fluoride salts, the lower LD_{50} values reflect the higher toxicity of the anion, rather than of the metal (c.f. NaCl and NaF in Table 11.1).

In Table 11.2, the acute oral toxicity of tin(II) chloride is compared with those of some other metal chlorides and it is of interest to note that there is no correlation between the toxicity of the metal (as its chloride) and the density. In accord with this, Luckey *et al.* have pointed out [25] that the toxicity of an element is a characteristic which is difficult to associate with groups in the Periodic Table.

A 2 year feeding study with tin(II) chloride in rats and mice has shown that, at 2000 ppm, this compound was not carcinogenic in the test animals [26]. SnCl_2 demonstrated low cytotoxic effects when tested *in vitro* on an

Table 11.1 Acute oral toxicities of inorganic tin compounds (rats)

Compound	LD ₅₀ (mg kg ⁻¹) ^a	Ref.
ZnSnO ₃	>5000	18
ZnSn(OH) ₆	>5000	18
Na ₂ Sn(OH) ₆	4350	19
SnO ₂	>10 000	19
SnO	>10 000	19, 20
Sn(OCH ₂ CH ₂ O)	>10 000	20
Sn[OC(O)C(O)O]	3400	20
Sn[OC(O)CHEtBu] ₂	5870	20
SnSO ₄	2205	19
SnCl ₂ ·2H ₂ O	3190	21
SnCl ₂	700	22
SnF ₂	188.2	23
NaSn ₂ F ₅	573 and 221	21, 23
NaCl	3000	10
NaF	22	10

^aDose which kills 50% of test animals.**Table 11.2** Acute oral toxicities of metals, as chlorides, and densities of metallic elements

Metal chloride (MCl _n)	LD ₅₀ (rats) ^a (mg kg ⁻¹)	Density of M ^b (cm ⁻³)
BeCl ₃	86	1.85
LaCl ₃	4184	6.15
ZrCl ₄	1688	6.49
SbCl ₅	1115	6.68
CeCl ₃	2111	6.69
CrCl ₃ ·6H ₂ O	1790	7.20
SnCl ₂	700 ^c	7.28
SnCl ₂ ·2H ₂ O	3190 ^d	7.28
FeCl ₂ ·4H ₂ O	984	7.86
CdCl ₂	88	8.64
HgCl ₂	1	13.55

^aRef. 10; ^bRef. 24; ^cRef. 22; ^dRef. 21.

established hamster fibroblast line [27]. Mutagenicity (genotoxicity) studies on SnCl₄ [28–31], SnCl₂ [28, 31–33], Na₂Sn(OH)₆ [31] and SnSO₄ [31] have, with only one exception [32], given negative results and SnCl₂·2H₂O and SnCl₄·5H₂O have been found in recent studies not to cause breakage of λ-DNA in the absence of hydrogen peroxide [34]. Teratogenic effects are not associated with inorganic tin [35].

In the UK, the legal general maximum limit for tin in food is 200 mg kg⁻¹ [36], compared with a much lower value of 1 mg kg⁻¹ for lead [37]. The no observed adverse effect level (NOAEL; the highest dose or concentration of a chemical in a single study, found by experiment or observation, that causes no detectable adverse health effect) for tin in a long term feeding study in rats was 20 mg kg⁻¹ bodyweight per day [35].

Tin is not included in the tables of inorganic chemicals of health significance in drinking water in the World Health Organization (WHO)

Guidelines for Drinking Water Quality, since its presence in the inorganic form does not represent a hazard to human health [35]. Tin levels in drinking water $>1\text{--}2\ \mu\text{g l}^{-1}$ are exceptional [35].

Tin(IV) chloride and tin(II) chloride display a low biological activity towards freshwater algae (Table 11.3) and, interestingly, inorganic tin salts have been reported to stimulate the growth of certain algae [40]. These compounds display a higher toxicity towards diatoms [41]. The 28-day LC_{50} value for metallic tin to rainbow trout is $0.42\ \text{ppm}$ [11].

In air, the generally accepted occupational exposure standard for tin and inorganic tin compounds except SnH_4 , is a threshold limit value (time-weighted average) of $2.0(\text{mg tin})\text{m}^{-3}$ [42]. The threshold limit value for tin and its compounds (together with As, Co, Cr, Cu, Mn, Ni, Pb, Sb and V) in the flue gases of incineration plants in European Community Council Directive 94/67/EC is $1.0(\text{mg metal})\text{m}^{-3}$ [43, 44].

11.3 Organotin compounds

The economically important tributyl-, triphenyl- and dibutyltin compounds [45] have a moderate toxicity [46] and have been used worldwide for over 30 years with few undesirable effects reported in humans [2, 13, 14, 47, 48]. In addition, there is a significant number of organotins which are practically non-toxic [46], including trioctyl-, dioctyl- and certain dimethyltin derivatives. Trimethyl- and triethyltin salts, in contrast, have a substantial acute toxicity [46] and, whilst these are not utilized commercially – but are occasionally employed in small quantities in academic and related research laboratories – there have been past occurrences of human fatalities involving exposure to them [2, 46]. Mild cases of poisoning, however, both in animals and in humans are reported to recover completely [46]. The acute oral LD_{50} values of a series of triorganotin acetates in rats are summarized in Table 11.4, the anionic moiety having little influence on the toxicity.

The LD_{50} values for some common dialkyltin compounds are listed in Table 11.5. The mono-organotin compounds have a low toxicity [45] and do not appear to have any important biological action in mammals.

Table 11.3 Toxicity of SnCl_4 and SnCl_2 to freshwater algae

Alga	$\text{IC}_{50}\ (\text{mg l}^{-1})^a$		Ref.
	SnCl_4	SnCl_2	
<i>A. falcatus</i>	12	14	38
<i>S. quadricauda</i>	>50	>50	38
<i>A. flos-aquae</i>	>5	>5	38
Lake Ontario algae	>50	>50	38
<i>P. malhamensis</i>	913^b	–	39

^aConcentration which effectively inhibits 50% of function/growth.

^b $\text{LC}_{72\text{h}}$.

Table 11.4 Acute oral toxicities of $R_3SnOCOMe$ (rats)

R	LD ₅₀ (mg kg ⁻¹)	Ref.
Me	9.1	49
Et	4.0	49
Pr	118.3	49
Pr ⁱ	44.1	49
Bu	125–136	50
Oct	30 000	10
cyclo-C ₆ H ₁₁	178	10
PhCMe ₂ CH ₂	2750	10
Ph	125–150	51

Table 11.5 Acute oral toxicities of R_3SnX_2 compounds (rats) [52]

Compound	LD ₅₀ (mg kg ⁻¹)
Me ₂ SnCl ₂	237
Me ₂ Sn[SCH ₂ C(O)O iso-Oct] ₂	1380
Et ₂ SnCl ₂	66
Bu ₂ SnCl ₂	219
Bu ₂ SnO	520
Bu ₂ Sn[SCH ₂ C(O)O isoOct] ₂	1037
Oct ₂ SnCl ₂	7000
Oct ₂ Sn[SCH ₂ C(O)O iso-Oct] ₂	2100

There is no conclusive evidence that organotin compounds are carcinogenic in animal studies [12, 13, 35] (Table 11.6) and many dialkyltin complexes are currently being investigated for their anticancer properties [60, 61] (Chapter 10).

Mutagenicity investigations on bis(tributyltin) oxide [13, 35] have largely given negative results, whilst the results on other organotin compounds have been mixed (Table 11.7).

Bis(tributyltin) oxide is not considered to be teratogenic in rats at oral doses below those producing maternal toxicity. The lowest no observed effect level with regard to embryotoxicity and foetotoxicity was 1 mg kg⁻¹ body-weight [13]. Teratogenicity studies on some dialkyltin compounds by Ema *et*

Table 11.6 Carcinogenicity studies of organotin compounds

Compound	Test study	Result	Ref.
Bu ₂ Sn(OCOMe) ₂	78 weeks feeding (rats and mice)	No conclusive evidence for carcinogenesis	53
(Bu ₃ Sn) ₂ O	106 weeks feeding (rats)	No compound-related tumours found [2]	54
Bu ₃ SnF	6 months dermal (mice)	Negative	55
Ph ₃ SnOH	78 weeks feeding (rats and mice)	Negative	56
Ph ₃ SnOCOMe	78 weeks feeding (mice)	Negative	57
cyclo-(C ₆ H ₁₁) ₃ SnOH	2 years feeding (rats)	Negative	58
(PhMe ₂ CCH ₂) ₃ Sn-O-Sn(CH ₂ CMe ₂ Ph) ₃	18 months feeding (mice)	Negative	59

Table 11.7 Mutagenicity studies on some organotin compounds

Compound	Test study	Ref.
MeSn[SCH ₂ C(O)O iso-Oct] ₃	Negative	62
BuSnCl ₃	Positive	29, 30
BuSn(O)OH	Positive	29, 30
PhSnCl ₃	Negative	29, 30
Me ₂ SnCl ₂	Positive	29, 30
Bu ₂ SnCl ₂	Positive	29, 30
Oct ₂ Sn[SCH ₂ C(O)O iso-Oct] ₂	Positive	63
[Oct ₂ Sn(maleate)] _n	Negative	63
Ph ₂ SnCl ₂	Negative	29, 30
Me ₃ SnCl	Negative	29, 30
Bu ₃ SnCl	Positive	29, 30
Ph ₃ SnCl	Negative	29, 30
Ph ₃ SnOH	Negative	62
Me ₄ Sn	Negative	29, 30
Bu ₄ Sn	Negative	29, 30
Bu ₄ Sn	Positive	64
Ph ₄ Sn	Negative	29, 30

al. [65] and by Noda *et al.* [66] suggest day 7 and/or 8 of pregnancy of rats to be especially susceptible to a single low level (*c.* 5 mg kg⁻¹) dose of dibutyltin compounds [67].

Acceptable daily intake (ADI) and Tolerable Daily Intake (TDI) values for the industrially used triorganotin fungicides and acaricides are shown in Table 11.8. For the non-commercial trimethyltin derivatives, Aldridge has predicted that the limiting dose for humans will approximate to no more than 1 mg (kg week)⁻¹ and, in practice, will have to be much less [2].

Exposure of the skin and by inhalation should be avoided for organotin derivatives [2]; the occupational limit for these compounds in air in many countries is 0.1 (mg tin) m⁻³ [13]. Some acute dermal and inhalation toxicities in rats are given in Table 11.9.

In drinking water, the WHO guideline value (GV), i.e. the concentration of

Table 11.8 ADI and TDI values for triorganotin pesticides

Compound	ADI ^a (mg (kg bodyweight) ⁻¹ day ⁻¹)	Ref.
Ph ₃ SnX	0.0005	68
(PhMe ₂ CCH ₂) ₃ Sn-O-Sn(CH ₂ CMe ₂ Ph) ₃	0.03	68
cyclo-(C ₆ H ₁₁) ₃ SnOH	0.001	68
1-cyclo-(C ₆ H ₁₁) ₃ Sn(1,2,4-triazole)	0.001	68
Bu ₃ SnX	0.0006	69
(Bu ₃ Sn) ₂ O	0.0016 (TDI ^b)	15
(Bu ₃ Sn) ₂ O	0.00025–0.005 (TDI ^b)	70

^aThe amount of a chemical which can be consumed every day for an individual's entire lifespan, with the practical certainty, based on all the available evidence, that no harm will result.

^bThe amount of a substance in food or in drinking water that can be ingested over a lifetime without appreciable health risk.

Table 11.9 Dermal and vapour inhalation toxicities for organotin compounds in rats [52, 68, 71]

Compound	Acute dermal LD ₅₀ (mg kg ⁻¹)	LC ₅₀ [(mg vapour) l ⁻¹]
MeSnCl ₃	–	600
Me ₂ SnCl ₂	–	>1.91
Bu ₃ SnCl ₂	–	73
OC ₂ Sn[SCH ₂ C(O)O iso-Oct] ₂	2250	–
(Bu ₃ Sn) ₂ O	505	0.077
Ph ₃ SnOCOMe	450	0.044–0.069
Ph ₃ SnOH	1600	0.060
(PhMe ₂ CCH ₂) ₃ Sn-O-Sn(CH ₂ CMe ₂ Ph) ₃	>1000	–
1-cyclo-(C ₆ H ₁₁) ₃ Sn(1,2,4-triazole)	>5000	–

a constituent that does not result in any significant risk to the health of the consumer over a lifetime of consumption, is 2 µg l⁻¹ for bis(tributyltin) oxide [35].

Tributyltin compounds are highly toxic to aquatic organisms and this property has given rise to their use over many years as biocidal ingredients in marine antifouling paints [45]. Studies carried out over the last 10–15 years, however, have revealed that they can induce calcification anomalies in the Pacific oyster, *C. gigas*, at concentrations of <0.8 (ng tributyltin) l⁻¹ [72] and the development of male characteristics (imposex) in the female dogwhelk, *N. lapillus*, at levels ≤0.5 (ng tributyltin) l⁻¹ [73]. The natural concentration of elemental tin in seawater is 0.003 mg l⁻¹ [74]. These adverse effects on shellfish have led to restrictions in most countries on the use of triorganotin derivatives in antifouling paints for small boats (typically, <25 m in length), since elevated concentrations of tributyltin species have occurred in small, enclosed pleasure craft marinas. For large, ocean-going vessels, the tributyltin methacrylate–methyl methacrylate copolymer antifouling paint formulations are still universally employed [75] and have not given rise to any serious pollution problems. In 1990 the International Maritime Organization (IMO) recommended that the average release rates of these antifouling paints should not exceed 4 (µg organotin) cm⁻² day⁻¹ [76]. Monitoring studies in European, Japanese and US locations [77–81] have indicated that the control measures have been largely successful, with a reduction of tributyltin levels in water, sediment and in tissues of aquatic organisms. Investigations of the half-lives of tributyltin species in aquatic environments indicate that these are short (typically 1–3 weeks) whereas, in anoxic sediments, the degradation process is significantly slower [82].

The current economic benefits to the marine industry, including fuel savings, from the use of tributyltin copolymer antifouling paints have been estimated to be c. \$3000 million annually and this reduction in world fleet fuel consumption gives rise to a concomitant decrease in CO₂ and SO₂ emissions into the environment [78].

Tin, in the form of an alloy, may also have a role to play in fuel economics. Over the past 5–10 years, tin alloy-based fuel saving/exhaust emission gas

reduction devices which, in the form of porous metal alloy pellets, are inserted into the fuel line or, less commonly, into the fuel tank of either spark ignition or diesel engines (including boat engines), have entered the market [83–87]. Typical fuel savings claimed by the manufacturers for cars and heavy vehicles are in the range 5–10% [83, 84, 86], although test results reported have been both positive [83, 88] and negative [89, 90].

Methylation of inorganic tin and methyltin species in aquatic environments does not appear to be an important process in short term studies [79, 91] and it is chemically unlikely that tin could be biologically methylated to give toxicologically significant amounts of trimethyltin species [2]. In this context it is important to note that, whilst trimethyltin derivatives are highly toxic to mammals, as discussed earlier, their biological activities – and those of the other methyltins, $\text{Me}_n\text{SnX}_{4-n}$ ($n=1-4$) – against many aquatic organisms are relatively low [38, 41, 91–97].

11.4 Manufacturers of tin chemicals

The primary producers of organotin compounds, i.e. those which utilize a Sn–C bond-forming process, cooperate on a worldwide basis in the Organotin Environmental Programme (ORTEP) Association, which was formed in 1972, the aims of which are to promote and foster the dissemination of scientific and technical information on the environmental effects of organotin compounds [98]. Its member companies are listed below:

Acima Chemical Industries Ltd
Im Ochensand
9471 Buchs/SG
Switzerland

Akcros Chemicals
PO Box 1, Eccles
Manchester M30 0BH
UK

Barlöcher Italia SpA
Via San Colombano 62/A
20075 Lodi (Milano)
Italy

Ciba Additive GmbH
Postfach 1640, Chemiestraße
D-68619 Lampertheim, Hess 1
Germany

Organotin Chemie GmbH
Strasse der Wissenschaft 8
Postfach 1200
D-4400 Bitterfeld
Germany

Witco GmbH
Postfach 1620
Ernst Scheringstrasse 14
D-59180 Bergkamen
Germany

Cardinal Stabilisers Inc.
PO Box 345
Columbia
SC 29202
USA

Elf Atochem North America
2000, Market Street
Philadelphia
PA 19103-3222
USA

Morton International Inc,
2000, West Street
Cincinnati
OH 45215
USA

Akishima Chemical Industries Co.
Akishima Building 7-14
Nihonbashihoncho 1-chome
Chuo-ku, Tokyo
103 Japan

Asahi Denka Kogyo KK
2-13 Shirahata 5-chome
Urawa
Saitama
336 Japan

Hokko Chemical Industry Co.
Mitsui Building No 2,
4-4-20 Nihonbashi Hongoku-cho
Chuo-ku, Tokyo
103 Japan

Katsuta Kako KK
1150 Sezaki-cho, Soka-shi
Saitamaken
340 Japan

Koriyama Kasei Co.
1-176 Sasagawa
Koriyama City
Fukushima-ken
963-01 Japan

Kyodo Chemical Co.
38-5 5-Chome Kyodo
Setagaya-ku
Tokyo
156 Japan

Nitto Kasei Co.
17-14 Nishiawaji 3-chome
Higashiyodogawa-ku
Osaka
533 Japan

Sankyo Organic Chemicals Co.
788 Kuji
Takatsu-ku, Kawasaki
Kanagawa
213 Japan

Tokyo Fine Chemicals Co.
Natsushima-cho
Yokosuka
Kanagawa
237 Japan

Yoshitomi Pharmaceutical
Industries
1-6-7 Yushima Bunkyo-ku
Chuo-ku, Tokyo
113 Japan

Song Woun Industrial Co.
Song Woun Building
59-4 Banpo-Dong
Seocho-ku, Seoul 137-040
Korea

The major world manufacturers of inorganic tin chemicals are as follows (adapted from Ref. 99):

Alcan Chemicals Ltd
Chalfont Park
Gerrards Cross
Bucks SL9 0QB
UK

Keeling and Walker Ltd
Whieldon Road
Stoke-on-Trent,
Staffs ST4 4JA
UK

MRI Pty Ltd
Five Islands Road
Unanderra
NSW 2526
Australia

William Blythe & Co.
Church
Accrington
Lancs BB5 4PD
UK

Alpha Chemicals (Australia) Pty Ltd
18, Inman Road
Dee Why
NSW 2099
Australia

Durham Chemicals
Birtley
Chester-le-Street
County Durham DH3 1QX
UK

Rhône-Poulenc
25, Quai Paul Doumer
F-92408 Courbevoie
France

Joseph Storey & Co.
Heron Chemical Works
Lancs LA1 1QQ
UK

Th Goldschmidt AG
Goldschmidtstrasse 100,
Postfach 101461
D-4300 Essen 1
Germany

Cesbra Quimica
Três Poços
Volta Redonda-RJ
Brazil

Hoechst AG
Postfach 80 03 20
D-6230 Frankfurt 80
Germany

Madras Fluorine Ltd
83 Kamaraj Avenue
Adyar
Madras 600020
India

O. Barlöcher GmbH
Riesstrasse 16
D-8000 Munchen 50
Germany

Billiton BV
PO Box 38
Westervoortsedijk 67
Arnhem
Netherlands

Metalurgica del Nalon SA
La Felguera
Asturias
Spain

Elf Atochem North America
2000 Market Street
Philadelphia
PA 19103-3222
USA

Harshaw Corp.
1000 Harvard Avenue
Cleveland
OH 44109
USA

Magnesium Elektron Inc.
500 Point Breeze Road
Flemington
NJ 08822
USA

Allied Chemical Corp.
Morristown
NJ 07960
USA

Yunnan Tin Corp.
Gejiu City
Yunnan Province
People's Republic of China

Nihon Kagaku Sangyo Co.
2-20-5 Shitaya 2-chome
Taito-ku
Tokyo
110 Japan

Showa Denko KK
Nissho Building
1-2-2 Do-jima, Kita-ku
Osaka
530 Japan

Yamanaka Kagaku Kogyo KK
2-18-35, 18-Jyo
Yodogawa-ku
Osaka
532 Japan

Yotsuhata Kagaku Kogyo KK
Arafune Building
3-2-3 Kanda, Chiyoda-ku
Tokyo
100 Japan

Kishida Kagaku KK
1-6-9 Dosho-machi
Chuo-ku
Osaka
541 Japan

Showa Denko KK
1-13-9 Shiba Daimon
Minato-ku
Tokyo
105 Japan

Kisan Kinzoku Chemicals Co.
2-13-57 Nakajima
Nishi-yodogawa-ku
Osaka
555 Japan

Matsuno Seiyaku KK
2-41 Hirano-machi
Higashi-ku
Osaka
541 Japan

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12 Industrial uses of tin chemicals

C. J. EVANS

12.1 Introduction

Tin chemicals used in industry fall into two main classes: inorganic tin chemicals and organotin compounds which contain at least one bond between tin and carbon. Compounds containing an organic anion in the molecule, but not containing tin-carbon bonds, are here referred to as inorganic compounds. The applications of these two classes of compound tend to be separate although there is some overlap in a few cases. In recent years, the consumption of tin has fallen somewhat, but tin chemicals continue to be an important outlet for the metal and with some recent developments, for example in the field of fire retardants, this area of use may show some growth. In the Western world in 1990, tin chemicals accounted for about 24 000 tonnes of tin consumption out of a total of 194 000 tonnes [1]; the breakdown is shown in Table 12.1.

In its inorganic compounds, tin can appear in two oxidation states: stannous or tin(II) and stannic or tin(IV). Industrially important compounds of each type exist. The chemistry of inorganic tin chemicals has been reviewed in detail [2] and their preparation, properties and uses have been described [3]. Inorganic tin chemicals are generally made by reacting tin metal with oxygen or halogens, or by dissolving tin or tin(IV) oxide in acids. Industrially important tin chemicals include tin(IV) chloride, tin(IV) oxide, tin(II) chloride, tin(II) carboxylates, tin(II) octoate (properly termed tin(II) 2-ethylhexoate), tin(II) sulphate, tin(II) fluoroborate, sodium and potassium hydroxystannates and zinc stannate and hydroxystannate. Applications include electroplating, glass manufacture and treatment, ceramic glazes and pigments, heterogeneous catalysts, fire retardants and gas sensors.

The great majority of organotin compounds and all the industrially important ones, have tin in the +4 oxidation state, although a few are known which

Table 12.1 1990 Western world consumption of tin in chemicals

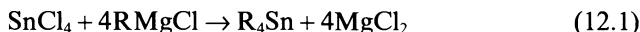
Application	Consumption (tonnes)
Ceramics industry	2 500
Glass industry	2 500
Plating	2 000
Catalysts	1 500
PVC stabilizers	10 000
Biocides	3 500
Other	2 000
Total	24 000

have tin in the +2 oxidation state. The number and nature of the organic groups attached to the tin atom dramatically affect the properties of the compound and especially the bio-activity. This allows properties to be tailored to a wide range of uses [4]. Tetraorganotins with four tin-carbon bonds are usually colourless liquids which are thermally stable to 200 °C; they have no significant commercial use except as precursors for other organotin compounds. Triorganotins with three tin-carbon bonds show high biocidal activity and hence find use as industrial biocides. Diorganotins, with two tin-carbon bonds, find use in the plastics industry as stabilizers and catalysts. Monoorganotin compounds have the lowest mammalian toxicity of the series and are used as synergistic additives with diorganotins to stabilize PVC. Because of their low toxicity, further industrial uses of these monoorganotins are being sought.

Tin(IV) chloride is usually the starting point for the manufacture of organotin compounds and the initial (and the most expensive) step involves the creation of direct tin-carbon bonds. The tetraorganotin is produced first and this is then reacted with more tin(IV) chloride to produce others in the series by a process of coproportionation. Derivatives are produced from these organotin chlorides for industrial end uses. Detailed accounts of the chemistry [5] and process technology [6] involved in organotin manufacture have been published.

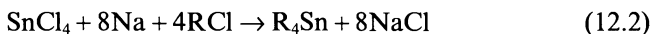
The main process routes are the following:

- Grignard method:



Mixed solvent systems are needed and large volumes are required, but the process is flexible with high yields. It is widely used and is the only feasible method of making phenyltin compounds.

- Wurtz method



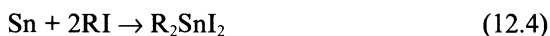
Again, large volumes of solvent are required; the main use is by one manufacturer in Germany [6].

- Aluminium alkyl method:



Since no solvents are needed, only a small reaction space is required and the process can be operated continuously. The presence of a complexing agent, such as an ether, is necessary for high efficiency. The method can be used to produce a wide range of tetraorganotins.

- Direct synthesis method



This process uses an alkyl iodide and a suitable catalyst and only dialkyltin species can be produced.

Coproportionation takes place with addition of further tin(IV) chloride:



Reaction products are separated by vacuum distillation.

Applications for organotin chemicals lie principally in PVC stabilization and as biocides, although there are some catalytic uses. In the case of tin chemicals, as elsewhere, environmental pressures are exerting an influence, but in some cases these are to the benefit of the market. For example, over 10000 tonnes of lead-based compounds are used for PVC stabilization; environmental dissatisfaction with lead could result in tin stabilizers picking up a considerable share of this market in the near future [7]. On the other hand, all biocidal compounds are coming under close scrutiny and whilst organotins still have a number of important uses in this sector, attempts are actively being made to find non-biocidal uses for them [8].

12.2 The plastics industry

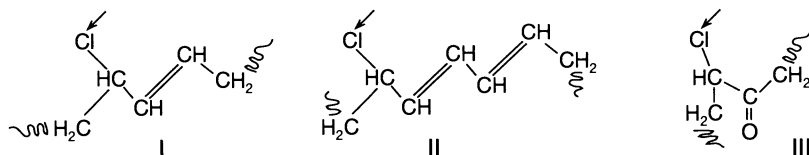
Tin chemicals, principally organotin compounds, are employed in a number of fields in the plastics industry, as stabilizers for poly(vinyl chloride) (PVC) and as catalysts for certain silicone elastomers and in the manufacture of polyurethane foam and polyesters.

12.2.1 PVC stabilization

PVC is the second most important plastic after polyethylene with demand currently running at over 4 million tonnes per year in Western Europe. Although it has been closely scrutinized on environmental grounds in recent years, a balanced study of all aspects, including incineration and recycling, reveals PVC to be an environmentally sound material with numerous benefits [9]. Its importance from the point of view of the tin chemicals industry lies in the fact that to be commercially viable, the plastic has to be protected against the degradative effects of heat and light and certain organotin compounds are amongst the most effective stabilizers known for the plastic.

During polymerization, the normal head-to-tail free radical reaction of vinyl chloride deviates from the usual path and this results in sites of lower chemical stability (defect sites) along some of the polymer chains. These defect sites are small in number and are formed by autoxidation, chain termi-

nation or chain branching reactions. Heat stabilizer technology has grown from efforts either to prevent chemically or to repair these defect sites. Typical defect sites occur in PVC homopolymers as shown in Scheme 12.1:



Scheme 12.1

The dissociation energies for the C–Cl bonds are significantly lower than that of a secondary C–Cl bond and can lead to thermal dehydrochlorination of the polymer backbone. The released HCl serves to catalyse further dehydrochlorination. As the conjugated polyene sequences grow in length, further weakening of the C–Cl bond occurs, leading eventually to rapid, catastrophic dehydrochlorination, cross-linking and chain scission, resulting in loss of mechanical, electrical and rheological properties in the final plastic. Discoloration appears with the colour changing to yellow, through brown and finally to black. Corresponding brittleness can also occur. Possible mechanisms of degradation have been extensively reviewed, for example in References 10–14.

Commercially important heat stabilizers are arrestive in nature; they chemically repair the defect sites or in some way reduce their deleterious nature during processing. They are also good scavengers for HCl; organotin mercaptides can absorb HCl:



etc.

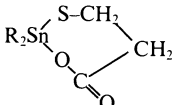
Carboxylate and mercaptide tin salts can also replace labile chlorine atoms, replacing them with more thermally stable C–O or C–S bound ligands. Organotin-based heat stabilizers are the most efficient and widely used PVC stabilizers, accounting for nearly 40% of the 64 000 tonnes of stabilizers used in the USA during 1992 [15]. Alkyltin mercaptides exhibit the highest overall heat stability and also impart excellent rheological properties to the polymer during processing.

The degradation of PVC by light has been less studied, although the subject is equally complex [16, 17]. Again, the presence of irregularities such as polyene sequences, initiator end groups and oxidation structures enables PVC to absorb light of longer wavelength and hence initiate degradation processes. Resistance to light and weathering is conferred by organotin carboxylates, although these generally confer poor rheological properties which can make processing difficult. The maleate is frequently used, often in its polymer form,

as poly(dibutyltin maleate). Mono- and dialkyltin compounds exert a synergistic stabilizing effect when used together and almost all organotin stabilizer systems are formulated with mixtures of monoalkyltin and dialkyltin species in a ratio calculated to maximize the stability of the PVC resin together with all the other microingredients in a given PVC formulation. Mercaptans are quite effective costabilizers for some of the alkyltin mercaptides [18]; such mixtures are currently regarded as the most efficient stabilizers for PVC extrusion processes. Lubricants can also enhance stabilizer performance and calcium stearate is a powerful costabilizer for the alkyltin mercaptides at a level of 0.2 to 0.7 phr (parts per hundred of resin). Calcium stearate can significantly improve early colour and increase the long term stability when present at low levels [15]. One company has introduced mixtures of tin mercaptides and tin carboxylates to produce a balance between thermal stability and weathering for transparent, outdoor applications [19]. Commercially important alkyltin stabilizers are listed in Table 12.2.

The main uses for organotin stabilizers are in packaging (blow-moulded bottles and clear sheet), building (extruded wall cladding, transparent sheet for rooflights and injection moulded pipes and pipe fittings), and miscellaneous applications (vinyl wall and floor coverings, cable insulation and coil-coated steel). In the packaging industry, the low toxicity and good leach resistance of certain organotin stabilizers have resulted in their use in PVC for food contact applications. Thus the FDA in the USA [20], BGA in Germany and JHPA in Japan have sanctioned the use of mixtures of dimethyltin and monomethyltin isooctyl thioglycolates, of di-*n*-octyltin and mono-*n*-octyltin isooctyl thioglycolates and of poly(di-*n*-octyltin) maleate as

Table 12.2 Commercially important alkyltin stabilizers

Compound	Formula	R
Dialkyltin diisooctylthioglycolate	$R_2Sn(SCH_2 \cdot COO \cdot C_8H_{17}^i)_2$	Methyl <i>n</i> -Butyl <i>n</i> -Octyl
Alkyltin tris(isooctylthioglycolate)	$RSn(SCH_2 \cdot COO \cdot C_8H_{17}^i)_3$	Methyl <i>n</i> -Butyl <i>n</i> -Octyl
Dibutyltin β -mercaptopropionate	R_2Sn 	<i>n</i> -Butyl
Monobutyltin sulphide	$(C_4H_9SnS_{1.5})_4$	<i>n</i> -Butyl
Dialkyltin maleate	$[R_2Sn \cdot OOC \cdot CH=CH \cdot COO]_n$	<i>n</i> -Butyl <i>n</i> -Octyl
Dialkyltin maleate ester	$R_2Sn(OOC \cdot CH=CH \cdot COOR)_2$	<i>n</i> -Butyl <i>n</i> -Octyl
Dialkyltin dilaurate	$R_2Sn(OOC \cdot C_{11}H_{23})_2$	<i>n</i> -Butyl <i>n</i> -Octyl

primary heat stabilizers for PVC in food packaging. The extreme clarity which can be obtained in PVC bottles and thin films with organotin heat stabilizers makes them the preferred additive for these products [21] (Figure 12.1). Concern about possible European legislation is encouraging development of non-toxic stabilizers to replace lead and barium/cadmium compounds, particularly for cable and cellular PVC. It is reported [22] that Morton International of Cincinnati, USA is keen to promote its methyltin mercaptoester sulphide stabilizer in Japan for PVC potable water pipes. These developments could lead to an expansion of the organotin stabilizer market. Applications of tin-stabilized PVC in the building industry have been summarized [23].

12.2.2 *Homogeneous catalysts*

A number of tin chemicals have important uses as homogeneous catalysts in the plastics industry. A homogeneous catalyst is one which is in the same phase as the reactants and is usually a liquid. The compounds most widely



Figure 12.1 Organotin stabilizers provide excellent clarity for PVC containers to be used in food-contact applications. (Photograph courtesy: Smiths Containers Ltd, Northants, UK).

used are stannous octoate (properly termed tin(II) 2-ethylhexoate) and various mono- and diorganotin compounds. These catalysts have an important role in the formation of polyurethane foams, in the production of polyesters and in the curing of certain types of silicone resins.

Polyurethanes are produced by reacting long-chain polyols (based on either polyethers or polyesters) with an aromatic diisocyanate to form a polymer with $-\text{CO}\cdot\text{NH}_2-$ linkages. Initially, polyurethane foams were produced by a two-stage process: in the first step a polyurethane was formed with terminal isocyanate groups, whilst in the second step water was added to react with these isocyanate end groups to form carbon dioxide gas which blows the polymer out into a foam. It was soon discovered that tin catalysts were able to catalyse the first step to such an extent that the whole process could be carried out in a single-stage 'one-shot' reaction, in which the curing time of the polymer matched the maximum expansion of the foam produced by gas evolution. The process has been described by Karpel [24]. About 800 tonnes of tin are used annually for polyurethane manufacture. Tin chemicals and tertiary amines are often used together in catalyst systems, and in these cases a synergistic effect is observed. Rusch and Raden [25] consider that the tin compound activates both the polyol and the isocyanate, first by the formation of a binary complex between catalyst and polyol, then by joining the isocyanate to form a ternary or bridge complex. This complex still allows the tertiary amine to approach in order to exert its catalytic effect. Amine-tin synergism is thought to be due to the extra stability of this activated intermediate complex of polyol, isocyanate, tin compound and amine.

Stannous octoate is widely used in flexible polyurethane foams, particularly the continuously produced 'slab' type based on polyether-type polyols. Dibutyltin dilaurate is employed in some specialized 'high-resilience' flexible foams and also in certain rigid foams, elastomers and coatings. Tin-based catalysts are usually employed in conjunction with amine cocatalysts at a level of about 0.1–0.4 phr. Flexible foam can be produced using either slab or moulding techniques. Continuously generated foam is ideal for conversion into bedding, upholstery, textile linings, etc., whilst moulding techniques where the reactants are injected into a closed metal mould are more suited to mass production of precise shapes such as car seats.

Traditional methods for slab foam production involve feeding all the constituents into a mixing head from where the reacting mixture is laid down in a conveyORIZED, paper-lined trough. As the reacting constituents are carried away horizontally, they produce the fully expanded polyurethane foam in a continuous block, typically 2 m wide and 1.2 m high. The block is cut into sections and stored for at least 12 h to enable it to cool down after the exothermic reaction. In reaction injection moulding, which employs a more reactive foam formulation the polymer mix is dispensed into preheated metal moulds and then hot-cured. Total cycle time may be as little as 20 min. High-resilience cold-cure formulations do not require heat for curing and hence

involve lower energy consumption. Rigid foams which are more highly crosslinked are widely used for insulation and for structural panels but tin chemicals have only limited application in these systems, dibutyltin dilaurate occasionally being used at very low (up to 0.1 phr) levels.

The polyurethane foam industry has had to meet strict environmental conditions in recent years particularly with regard to auxiliary blowing agents of the kind needed to produce soft low density foams. CFCs had been commonly used but these are being phased out and alternative systems such as water-blown formulations are being developed [26]. New developments in flexible foam processing have been described [27, 28]. These include the 'Vertifoam' process developed by Vertifoam International Ltd of Glossop UK, in which the foam is conveyed vertically rather than horizontally and the 'Hypercure' system developed by the same company which reduces the cool/cure time for the foam from 12–18 h down to 20–40 min (Figure 12.2).

Another application for tin chemicals is as curing agents for room temperature vulcanizing (RTV) silicones. Silicones are polymeric materials based on the inorganic siloxane backbone $(-\text{Si}-\text{O}-)_n$, the other valencies on the silicon atom usually being taken up by organic groups or by hydrogen. Silicones may be produced in the form of resins, oils, gums, elastomers, pastes, etc., but

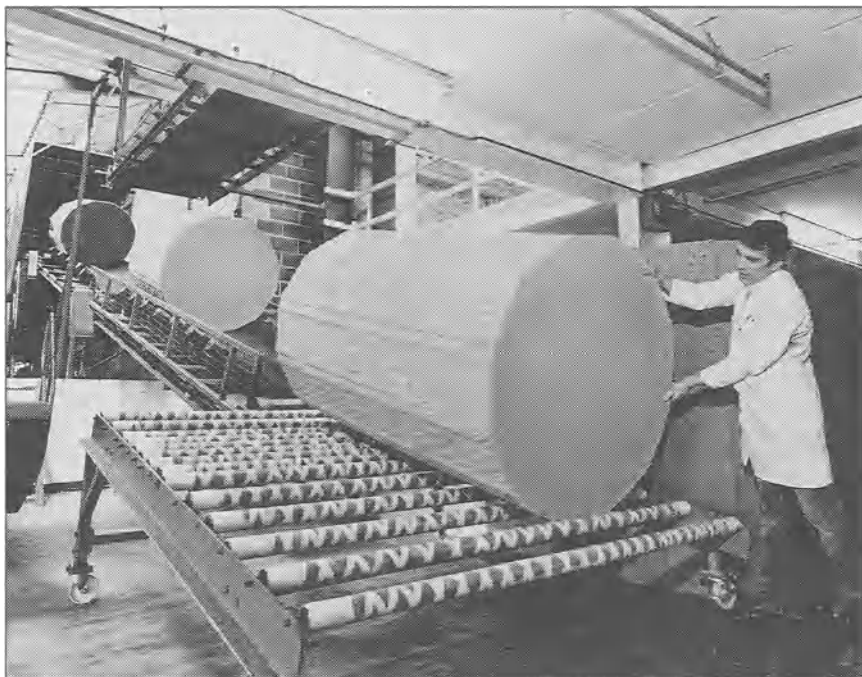


Figure 12.2 Circular cross-section polyurethane foam blocks descending to ground level in the Vertifoam process. (ITRI Ltd. Photograph courtesy Vertifoam International Ltd.)

the products in which tin-based catalysts find use are liquids which are fluid enough to be easily spread or poured and which subsequently cure at room temperature under the influence of a catalyst, to tough elastomeric solids. Organotin compounds used in this field include dibutyltin dilaurate and to a lesser extent, dibutyltin octoate and stannous octoate. The catalyst may be incorporated at a level of 0.1–1.0% with the rate of curing controllable to some extent by the catalyst concentration. The chemistry of these compounds and their characteristics and uses have been described [29, 30]. The curing reaction can consist of condensation or addition processes. Whereas a platinum-based catalyst is normally used in addition processes, the tin compounds are extensively used in condensation systems. In these, polydialkyl siloxanes are used which have terminal hydroxyl groups on the chains; these can react with a cross-linking agent, namely a tetraalkoxysilane, in the presence of a catalyst. Four chains thus become linked via new siloxane bonds with an alcohol evolved as a by-product. Research into the mechanism by which tin chemicals catalyse the condensation reaction suggests that the actual catalyst is a hydrolysis product (dialkyltin hydroxycarboxylate), the catalyst being regenerated as polymerization proceeds [31].

RTV silicones are available as either two-pack or one-pack systems. In two-pack systems, one of the components contains the catalyst and reaction commences on mixing. In one-pack systems, reactive groups are blocked off until contact with moisture in the atmosphere frees them for subsequent reaction. Applications include encapsulation and potting of electronic components, sealing and caulking, non-stick coatings on paper and moulding and casting. RTV silicones are much used in model making and can provide accurate replication in medical and other applications. One example concerns the use of an RTV silicone to preserve the imprint of the world's oldest language discovered on a 5000 year old clay tablet in Uruk, Southern Iraq [32].

Dibutyltin dilaurate and dibutyltin oxide are used as catalysts in esterification and transesterification reactions, for example in the manufacture of dioctylphthalate and other phthalates, fatty acid esters, unsaturated and saturated polyesters and polyester diols. They are commonly used at a level of about 0.1–0.2%. The possibilities of monoorganotin compounds as esterification and transesterification catalysts have also been examined [33]. In the USA, the FDA has recently sanctioned the use of three organotin catalysts for food contact applications, e.g. equipment for the preparation and serving of food [34]. Stannous octoate and dibutyltin carboxylates are also used to catalyse condensation and addition reactions as in the manufacture of alkylid resins and rosin esters. Other systems in which tin compounds have been used as homogeneous catalysts include the preparation of organic silicate binders in the foundry industry [35], Friedel–Crafts alkylation and acylation, etherification [36], and liquid-phase hydrogenation, dehydrogenation and isomerization [3].

12.3 Glass and ceramics

Tin chemicals, principally tin(IV) oxide, are used in the glass industry both to manufacture certain types of glass and also to confer special properties to glass surfaces [37]. In the ceramics field, tin(IV) oxide is included in several pigments and glazes and this traditional use has been revitalized by the development of new coloured pigments. Total use of tin in these two areas has been estimated at about 5000 tonnes [1].

12.3.1 *Glass melting*

Tin(IV) oxide electrodes are used in the manufacture of lead-containing crystal glass by electric melting, the preferred technique on environmental grounds. Glass melts do not become electrically conductive until the temperature rises above about 800 °C, but once this temperature is exceeded, the melt can support an electric current and resistance heating can take place via electrodes inserted into the glass melt. Conventional electrodes for glass melting furnaces are made of molybdenum or graphite but these are not suitable when the glass melt contains 12% or more of lead. Compressed tin(IV) oxide electrodes are now in general use for this process. These electrodes, in the form of cylinders or blocks weighing between 5 and 50 kg, are made either by slip casting or by isostatic pressing followed by sintering to high density. The electrical conductivity of tin(IV) oxide increases with increasing temperature and in order to enable the electrode to conduct current from the cooler, outer part to the end immersed in the molten glass, it is coated with silver or fitted with silver inserts. This application has been fully described [38, 39].

12.3.2 *Coatings on glass*

Thin coatings of tin(IV) oxide on glass have a number of uses. Thinner coatings, up to 100 nm thick, are used to strengthen glassware subjected to rigorous use and returnable bottles and jars. The coating is applied to the freshly made glass surface and results in a considerable increase in impact resistance, so that lighter and cheaper vessels can be produced with no loss in performance. The tin(IV) oxide coating also assists in the adherence of an organic lubricant film which is applied to improve the scuff resistance of the glassware. These strengthening treatments have been described [40, 41]. The precursor for these tin(IV) oxide films was originally tin(IV) chloride applied in vapour form to the hot (typically 500–600 °C) glass surface where it pyrolyses to tin(IV) oxide. A newer process employs *n*-butyltin trichloride as precursor [42]. The monoorganotin is vaporized and applied to the surface of the hot glass under a specially designed double-loop coating hood that reduces vapour losses. Use of this organotin precursor is claimed to eliminate

problems with fuming and with corrosion of equipment experienced occasionally when using tin(IV) chloride.

If the tin(IV) oxide layer is thicker, of the same order as the wavelength of visible light (100–1000 nm), interference effects confer an iridescent appearance on the glass surface and this has been exploited for decorative purposes [43]. However, greater interest is currently being shown in thicker films, greater than 1 μm thick, which, although still optically transparent, are electrically conductive. Pure tin(IV) oxide is an insulator, but the introduction of various doping elements can turn it into either a p-type or an n-type semiconductor or into a normal electrical conductor. There are two main types of conductive film incorporating tin(IV) oxide: the first utilizes the pure oxide which has been doped with a small amount of another element [44], whilst the second is 'indium–tin oxide' (ITO) where the tin is normally the minor constituent in the matrix. The latter type is costlier and less durable, but is more easily etched chemically and hence may be preferred when complex conductive patterns are required [45]. Applications of these films have been reviewed [46] and include self-deicing windscreens for aircraft, transparent tube furnaces, security alarm glazing, electroluminescent display systems [47, 48] and electrical field shielding material [49].

Tin(IV) oxide-coated glass and screen-printed frit lines are commonly used in combination in doors of supermarket freezers to keep them free of condensation, allowing shoppers to see inside [50]. Tin(IV) oxide also figures in some low emissivity glass panes for windows and doors. These panes, carrying a thin oxide film, reflect and retain indoor heat in winter and reduce solar heat gain in the summer, and are proving increasingly popular in both residential and office buildings. In this connection, a powder pyrolysis technique has been described [51] for applying thick tin(IV) oxide coatings directly on a float glass line.

The current literature contains a great many papers describing methods for producing thin tin(IV) oxide or tin–indium coatings, many of them producing coatings with special properties. Four main techniques are employed, namely chemical vapour deposition [52, 53], spray deposition [54], vacuum evaporation [55] and sputtering [56, 57]. A pulsed laser has been used for deposition of indium–tin oxide films on glass. Resistivity of these films compared well with the best published values at high deposition temperatures [58]. Tin(IV) oxide thin films have also been produced by 'sol–gel' methods [59].

12.3.3 *Tin(IV) oxide in the ceramics industry*

The ceramics industry has provided one of the oldest uses of tin chemicals and this traditional application continues today. Anhydrous tin(IV) oxide has served as an opacifier in ceramic glazes since ancient times. Tin(IV) oxide is highly insoluble in glazes and provides a high opacifying power when

present at concentrations of 4–8%. Although challenged today by cheaper alternative materials, it is still the preferred additive for high quality artware and for those industrial applications where the highest reflectivity, purest colours, greatest strength and abrasion resistance are required. Particle size is very important with the highest reflectance occurring with particles of 0.2–0.3 μm diameter [60].

The rutile-type structure of tin(IV) oxide is also able to accommodate certain metal colorant ions in the lattice and this property is responsible for the largest use of tin(IV) oxide in the ceramics industry [61, 62]. There are three series of commercial pigments based on this system and these are used for ceramic tiles and pottery (Figure 12.3). Tin–vanadium yellows containing 2–5% vanadium and tin–antimony blue-greys containing 3–3% antimony are prepared by thermal reaction at 1200–1300 °C between tin(IV) oxide and either ammonium vanadate or antimony trioxide. A third series, the



Figure 12.3 Ceramic decoration based on tin(IV) oxide-containing pigments (ITRI Ltd).

chromium–tin pinks, are prepared by firing a mixture of SnO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, CaCO_3 and SiO_2 at 1150°C ; the colour can vary from maroon to light pink, and the host lattice is believed to be malayaite [63]. Work has been described [64] which is aimed at widening the scope of chrome–tin pinks by developing lead-free glazes suitable for this pigment. Attempts have been made to incorporate other potential colorant ions into a rutile-type host lattice; other oxidic lattices have also been explored as hosts. Although much of this work has thrown new light on the structure and mode of action of these pigments, no new colours have to date reached commercialization. Advances in ceramic colour research have been described by Airey [65].

The tin-based pigments have outstanding thermal stability and can be used under glazes without danger of discoloration at the high glazing temperature. They also find use as glaze stains, the pigment being mixed with the glaze to produce all-over coloration, for example on ceramic tiles and on sanitary ware. Certain tin pigments also have potential in vitreous enamelling. The ancient pigment known as ‘Purple of Cassius’ also contains tin. It can be prepared by the aqueous reduction of gold(III) chloride by tin(II) chloride, to produce a colloidal dispersion of metallic gold on hydrous tin(IV) oxide [66]. Although expensive, this pigment is still used as an on-glaze decoration for high quality tableware, due its unsurpassed clarity and brightness.

12.4 Electroplating

A viable process for electrodeposition of tin from an alkaline stannate bath was first developed in the 1930s, and since that time the importance of tin and tin alloy electrodeposits has steadily grown, so that today, plating represents the largest single use for inorganic tin chemicals. The most commonly used compounds are tin(II) sulphate, tin(II) chloride, tin(II) fluoroborate and sodium and potassium stannates. These are used to produce a range of deposits containing tin, generally on metallic substrates. The most important coatings are tin itself (used particularly in the manufacture of tinplate and in electronics) and tin–lead (used chiefly in electronics). Other coatings include tin–nickel, tin–zinc, tin–copper, tin–cadmium and tin–cobalt. Reviews of tin and tin alloy plating have been published [67–69]. Coatings are possible in the thickness range $2.5\text{--}75\text{ }\mu\text{m}$, depending on the deposit. Characteristics of tin and tin alloy electrodeposits are summarized in Table 12.3.

12.4.1 Tin plating

There are two principal types of bath used for tin plating: alkaline baths and acid baths [70]. Alkaline systems employ sodium or potassium stannates as electrolyte with free sodium or potassium hydroxide. A limitation of this system is the need to operate it hot ($70\text{--}80^\circ\text{C}$); in addition, operating current

Table 12.3 Summary of tin and tin alloy electroplating processes

Deposit	Electrolyte	Characteristics and applications
Tin	Alkaline bath: sodium or potassium stannate, free hydroxide, 80 °C; tin anodes Acid bath: tin(II) sulphate, free sulphuric acid, cresolsulphonic acid, addition agents, room temperature Bright tin: acid sulphate bath plus addition agents as brighteners	Matt coatings which are soft, ductile, solderable and corrosion resistant. Used for electrical parts and general consumer goods Somewhat harder and less ductile than matt deposits, used for decorative applications and electronics components
Tin-lead	Tin(II) fluoroborate, lead fluoroborate, free fluoroboric acid, addition agent, room temperature; tin-lead anodes Fluoride-free bath: tin(II) and lead alkylsulphonates	Tin and lead can be deposited in any proportion and deposits are fine grained. Mainly used in the electronics industry More environmentally friendly bath
Tin-nickel	Tin(II) chloride, nickel chloride, ammonium bifluoride, 70 °C; anodes can be tin-nickel alloy, separate nickel and tin, or nickel Bright tin-nickel: tin(II) chloride, nickel chloride, ammonium chloride, brightening agent, 60–70 °C; nickel anodes	Brightness depends on the quality of the substrate. Hard, rather brittle, corrosion-resistant and wear-resistant deposit. Used in decorative applications, consumer goods and parts of laboratory equipment where tarnish resistance is an advantage Bright deposits, the brightness and colour being uniform over a wide current density range
Tin-zinc	Cyanide-free bath: sodium zincate, sodium stannate, free caustic soda, complexant/stabilizer brightener and grain refiners, 60–70 °C; filmed tin-zinc alloy anodes	Tin-zinc alloys can be produced in all proportions, semi-bright when required, fine grained and essentially pore free. Good corrosion protection for steel and other metal substrates. Used on electrical and electronic apparatus and on automotive parts (with a passivation treatment)
Tin-copper	Sodium or potassium stannate, copper cyanide, free hydroxide and free cyanide, 60 °C; anodes usually cast 10% tin bronze	Bath has a very high throwing power and deposits are hard, very wear resistant. Used on moving parts of hydraulic systems (such as pit props) and as a decorative coating
Tin-cobalt	Cobalt sulphate, tin(II) sulphate, complexing agent, brightener	Tin–20% cobalt deposits have a similar appearance to chromium. Wear resistance is less than for chromium, but solderability is very good

densities are relatively low, so that deposition is slower. Faster plating can be achieved when potassium salts are used. Advantages include high throwing power, which makes the bath suitable for plating fabricated articles and the fact that no addition agents are needed. Acid baths are based on tin(II) sulphate or tin(II) fluoroborate solutions. The acid sulphate system uses tin anodes and the bath contains tin(II) sulphate and free sulphuric acid as well as phenolsulphonic or cresolsulphonic acids to stabilize the bath against atmospheric oxidation, and organic addition agents such as gelatin and

β -naphthol to ensure smooth, fine-grained deposits. Current efficiencies approaching 100% are possible with this system in a static bath. Acid sulphate baths are extensively used for barrel plating of small parts. When plated, tin coatings are white and matt in appearance, but bright deposits can be obtained by including suitable proprietary brighteners in the bath. Tin(II) fluoroborate baths have good throwing power and covering power, provided suitable addition agents are present. Relatively high plating speeds are possible and the process is used for continuous plating of strip and wire [71]. Tin electrodeposits are soft (10–12 HV for matt, 15–20 HV for bright deposits), ductile, corrosion resistant, non-toxic and readily solderable. In addition to tinfoil manufacture, tin coatings are used on sieves, screws, can openers, etc., where they have a protective role, and in contact with food as on steel baking tins for bread. The electronics industry uses tin as a protective and easily soldered finish for radio chassis, computer frames, tags, connectors and printed circuit boards. Much of the copper wire used in the electrical industry is electroplated for solderability. Decorative items such as jewellery are also frequently bright-plated.

Attempts have been made to produce coatings with novel properties by incorporating non-metallic particles in tin or tin alloy electrodeposits by a process of codeposition [72]. Increased lubricity has been achieved in tin–molybdenum disulphide composites and good abrasion resistance in tin–silicon carbide and in tin–nickel/silicon carbide codeposits.

In addition to electroplating, immersion or electroless processes can be used to produce tin coatings. These processes usually depend on a simple replacement reaction in which atoms of the metal to be coated are replaced by tin atoms from the solution. A limitation of these systems is that as the metal surface becomes covered with tin, reaction slows down. However, Japanese workers have developed a method for producing electroless tin deposits without the use of a reducing agent, at rates up to $5\text{--}10\ \mu\text{m h}^{-1}$ [73]. The plating results from a disproportionation of the stannite ion and the solution is said to be stable for several months, provided the composition is controlled and the solution is filtered. Other processes have been described [74–76]. Immersion tinning is mainly used to assist lubricity [77] or to coat tags and printed circuit boards for short term interim protection.

12.4.2 Tin alloy plating

Perhaps the most widely used alloy coatings are those based on the tin–lead system. Tin–lead coatings are particularly useful in electronics assembly because during soldering they fuse, along with bulk solder, so that powerful fluxes are not needed. Martin and Toben [78] have examined the requirements of tin and tin–lead coatings for electronics applications. Although bright deposits can be produced using suitable additives, matt deposits are usually preferred for electronics applications and these are then subsequently

fused (the so-called hot air solder levelled or HASL coatings). Tin-lead alloys are customarily deposited from fluoroborate baths; depending on the proportions of tin(II) and lead fluoroborates present in the bath, a whole range of tin-lead alloys can be deposited [79]. Free fluoroboric acid is present to prevent hydrolysis and to improve conductivity; the anode is usually of the same composition as the alloy to be plated. For smooth deposits, addition agents such as peptone, bone glue or resorcinol are needed. Radovic [80] examined the possibility of using hydroquinone as an additive in place of peptone to produce alloys containing 7–10% tin for engineering applications. Increasing preoccupation with environmental considerations has led to the development of tin-lead baths which are fluoride free. Some of the most effective depend on the use of alkylsulphonates [78, 81]. These baths are claimed to offer other advantages such as excellent throwing power and low metal concentrations, resulting in improved metal distribution. Current developments with sulphonate-based baths have been reviewed by Fellmann [82]. Russian workers have recently described the development of a methane-sulphonic acid bath to produce bright tin-lead coatings containing 57–63% tin [83]. In addition to applications in electronics, tin-lead coatings are used in the manufacture of motor car radiators and in bearings applications. Terneplate (tin-lead-coated steel sheet) has been produced electrolytically in Germany in a continuous process. The electrolyte is based on fluoroborates and a lead-tin coating containing $9 \pm 2\%$ tin is produced on the line. Terneplate has applications in the building and engineering industries.

Tin-nickel coatings can be deposited from a bath containing tin(II) and nickel chlorides and ammonium bifluoride; ammonium chloride is also present as an anti-stress agent [84]. The anodes may consist of separate tin and nickel electrodes or an alloy of the metals. The coating consists of an intermetallic compound NiSn (67% tin, 33% nickel) and this composition is largely maintained over a fairly wide range of operating conditions. Tin-nickel alloy can be deposited on steel, copper, brass or nickel; for decorative purposes it is usually plated on polished brass. The coating is bright and non-tarnishing with good resistance to finger marking, and it remains bright indoors or outdoors even in polluted atmospheres. Tin-nickel coatings are hard (700 HV) and wear resistant, with good antifriction properties. A characteristic of the coating is that the electrolyte is not self-levelling and the brightness of the deposit follows that of the substrate. Decorative and functional applications have been described [85, 86] and include tubular furniture, taps, fittings and giftware. The coating has also been applied to panels used in solar energy conversion [87].

The scope of tin-nickel coatings has recently been widened by the introduction of modified plating baths. One such bath, trade named 'Nicostan 91' contains tin(II) chloride, nickel chloride, a fluorine compound and an addition agent whose composition has not been disclosed. The bath can operate up to 4.5 A dm^{-2} , allowing very high plating rates; the bath is also said to be

less corrosive to plating equipment and safer to handle [88]. Another bath with the trade name 'Eboni 2000', produces tin–nickel coatings with a dark, smoky appearance whilst maintaining the lustre of conventional coatings on a bright surface. This coating is currently being applied to golf club shafts over a nickel undercoat on steel [89].

The original bath for depositing tin–zinc coatings was based on the sodium stannate–zinc cyanide system; the deposit composition could be varied over the entire range by adjusting the cyanide or free alkali content [90]. The bath needed to be carefully monitored and a new cyanide-free bath has been developed which possesses several advantages over the earlier system [91]. This 'Stanecz' process employs a bath containing sodium or potassium stannate, sodium or potassium zincate, a complexing/stabilizing agent (not disclosed) and brightening and grain refining additions. The anode is a filmed tin–zinc alloy and mechanical agitation of the bath is an advantage. The composition of the deposit is adjusted by varying the amounts of zinc and free hydroxide in the bath; composition is relatively insensitive to tin content, current density or temperature. The bath allows semi-bright deposits to be produced when required and coloured passivation films can be applied to the coating for decorative purposes. A selection of possible finishes is shown in Figure 12.4. Tin–zinc coatings have good ductility, good frictional properties and wear resistance, especially when lubricated, and good solderability; hardness is 37 HV. The deposits combine the barrier protection afforded by tin with the galvanic protection characteristics of zinc. For all-round general performance, the optimum coating contains 70–80% tin, but higher zinc contents (50%) are recommended for structural steel susceptible to damage sites. Tin–zinc coatings have also been used to protect the frames of electronic and electrical apparatus and on critical automotive parts such as fuel and brakeline components and in other engineering applications. The possibilities of tin–zinc alloy plating as an alternative to cadmium coatings have been explored [92].

A number of other alloy coatings find limited use and these include copper–tin alloy. The electrolyte is a solution of sodium or potassium stannate with copper cyanide and a controlled excess of free alkali metal cyanide or alkali metal hydroxide. Compositions ranging from 7 to 98% tin can be obtained. The most important coatings are those containing 7–20% tin and the 40% tin coating known as 'Speculum' on account of its high reflectivity. Special addition agents have been developed which overcome previous limitations of the process [93]. Applications include protection of sliding parts against wear, costume jewellery, fittings and electrical contacts.

Tin–20% cobalt alloy coatings have a very similar appearance to chromium and have been successfully used as a thin coating over bright nickel. Wear resistance is less than that of chromium but solderability is better. Several baths have been described [69], but the one which has found most commercial success is a slightly alkaline sulphate bath containing cobalt

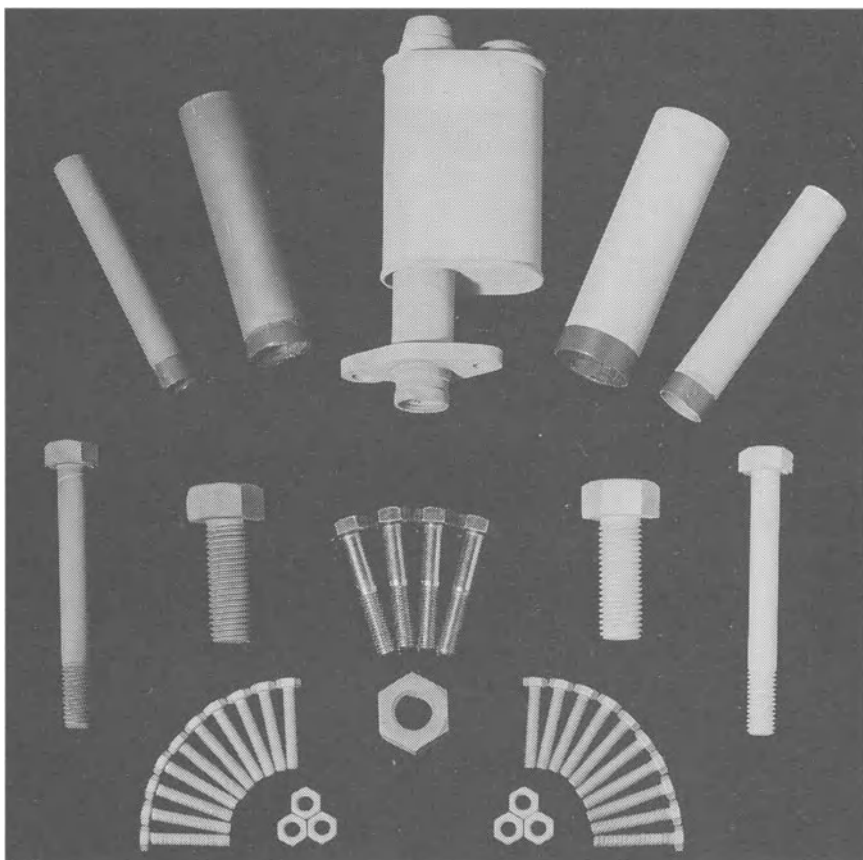


Figure 12.4 A selection of components plated by the new ITRI Ltd tin-zinc process, including matt, semi-bright and coloured passivated finishes (ITRI Ltd).

sulphate, tin(II) sulphate and a complexing agent which stabilizes cobalt and tin salts in the operating range. Close control of bath composition is essential in order to ensure a consistent colour in the coating. Tin-cobalt plating is used on many types of fastener, on hinges, hand tools, bathroom and kitchen fittings and tubular furniture.

12.5 Biocidal applications

Biocidal applications of organotin derivatives stemmed from a systematic study conducted in the 1950s at the Institute for Organic Chemistry, TNO, Utrecht, Holland. This established the powerful biocidal properties of the trialkyltin and triaryl tin compounds and it was not long before their commer-

cial possibilities were realised. Triphenyltin compounds were shown to have fungicidal activity combined with very low phytotoxicity, and in the late 1950s triphenyltin acetate was introduced commercially as an agrochemical, followed shortly afterwards by triphenyltin hydroxide. Since the 1960s other organotin compounds have been developed as agrochemicals. Other biocidal uses of triorganotin compounds became widespread and include wood preservation and antifouling paints for marine use; smaller outlets include disinfectants and algicidal treatments for building materials. Biocidal and other uses of organotin compounds have been reviewed [94, 95].

The toxicology of organotin compounds is very complex and has been extensively studied, especially by Aldridge [96, 97] and Selwyn [98]. Toxicity data on organotin compounds have been compiled by Smith [99], who has also examined the relationship between toxicity and structure for organotin compounds [4]. Progressive introduction of organic groups at the tin atom in any R_nSnX_{4-n} series produces a maximum biological activity at $n=3$, i.e. R_3SnX . The nature of the group X has little effect on the biological activity (unless the group is itself bioactive), but the organic group R does have some effect on the specificity of the compound against insects, mammals, bacteria, etc. Because of this, it has been possible to tailor the organotin biocide to meet the requirements of a specific application; for example, bis(tri-*n*-butyltin) oxide has been adopted as a wood preservative since it exhibits the widest separation between fungicidal activity and mammalian toxicity.

At this time of environmental awareness, all biocides are being closely studied. A number of comprehensive reviews have been published on the environmental impact of organotin compounds [99, 100]. The Ministry of Agriculture, Fisheries and Food in the UK has published detailed evaluations on bis(tri-*n*-butyltin) oxide used as a fungicide [101], and on triphenyltin hydroxide [102], triphenyltin acetate [103] and fenbutatin oxide [104] all used as pesticides. Certain restrictions have been placed on the use of triorganotin compounds in wood preservation and in antifouling paints. Provided due care is taken, no long term burden is likely to be posed by these uses. In 1978 the world's manufacturers of organotin compounds set up the Organotin Environmental Programme (ORTEP) Association. This body has the aim of promoting the dissemination of scientific and technical information on the environmental implications of using organotin compounds in order that these chemicals might be used in a responsible manner and in appropriate circumstances.

12.5.1 *Wood preservation*

An important use of organotin biocides is in wood preservation. Wood is an excellent structural material but it suffers from the limitation that, like all living things, it is susceptible to biodeterioration. Under certain conditions,

particularly warmth and damp, wood can be attacked by fungi of various types (the so-called wet and dry rots) and by wood boring insects such as the powder post beetle, the common furniture beetle and the death watch beetle. The consequences of such attack may range from an impairment of the appearance to actual structural damage. Modern buildings tend to be more susceptible to attack, due to the increased use of more vulnerable sapwood, rather than the more resistant heartwood, and the prevalence of central heating and the use of paint finishes which can prevent evaporation of moisture from damp external joinery timbers [105]. Fortunately there are chemicals which will destroy these fungi and kill or repel insect pests and these are the basis of curative or preventative treatments. Since 1959 an organotin compound, bis(tributyltin) oxide, commonly referred to as TBTO, has been used in many preservative formulations; other tributyltin compounds are also occasionally employed. TBTO is used at concentrations up to 3% in a solvent such as kerosene, usually in conjunction with a contact insecticide, for pretreatment of wood. In Britain, the level of TBTO is set by law at 1.5% maximum for professional treatments and at 1% maximum for domestic application. TBTO has several advantages for treating wood: it is a colourless liquid and hence does not colour the wood, it has low volatility and low water solubility, so that it is not easily leached from treated wood, and wood can be painted or glued in the normal fashion shortly after treatment. Other tributyltin compounds which find some use in wood preservation in various countries include the naphthenate, phosphate and benzoate. Some concern has been expressed about the possible harmful effects of these wood preservatives when they are applied *in situ*. In some cases these harmful effects have derived from the particular contact insecticide used in conjunction with the organotin. Provided precautions are followed and adequate time is allowed before habitation after treatment, no harmful results should arise. Certainly, TBTO has a long record of safe and successful use in wood preservation, extending over more than 30 years. The toxicology of TBTO has been examined by Schweinfurth [106] and there is a detailed MAFF report on the compound [101].

The technique of preservation involves getting the toxic agent into the structure of the wood, so that it can be effective against fungi or insects. Although still often applied by brushing or spraying, as in remedial treatments, pretreatments involved initially immersion of the wood and subsequently controlled vacuum and pressure impregnation techniques. A significant development was the introduction of a double vacuum process. In this treatment wood is first loaded into a treatment vessel and a vacuum applied; treatment solution is flooded into the vessel and the vacuum adjusted to allow a predetermined excess of solution to be absorbed by the timber. The treatment solution is then withdrawn from the chamber and the vacuum adjusted to remove excess solution from the wood. The vacuum is finally released and the timber, ready for further processing after only a short time,

is removed from the vessel. For timbers such as spruce, whose uptake and penetration are low, a pressurized immersion phase is introduced into the double vacuum schedule. These treatments have been described [107].

The development of these organotin-based preservatives and relevant research work have been summarized [108]. Standard wood test methods are used to assess the effectiveness of biocides in wood preservation. These consist essentially of exposing treated wood blocks to pure cultures of wood-destroying fungi. The culture medium is either agar or sterile soil. In both cases, blocks can be artificially weathered (for example by leaching with water) before exposure. The degree of decay is assessed by determining weight loss in the blocks and is related to the concentration of preservative in the wood. Much research has been conducted into mechanisms by which organotin preservatives exert their effect and in particular into factors influencing the duration of protection [109–112]. There is still some difference of opinion regarding the mechanism of protection, some workers favouring a protection of active sites on the wood cellulose molecule, others preferring intercellular attack on the fungus. Although there is some evidence that certain organisms can cause the breakdown of tributyltin compounds in the wood [113], protection is found to continue even when considerable amounts of the tributyltin compound have been dealkylated to dibutyltin or monobutyltin forms [114]. Some work has been concerned with introducing a bioactive group into the tributyltin molecule in order to enhance its activity. One study has examined *N,N*-dialkyldithiocarbamates as fungicides for wood preservation [115]. The fungicidal activity of a series of tri- and diorganotin compounds has been explored by Moens *et al.* [116].

The low aqueous solubility of TBTO and other commercially used tributyltin preservatives has restricted their industrial use in waterborne systems. One approach has been to make TBTO water-dispersible by the addition of suitable quaternary ammonium compounds (which themselves have some biological activity) [117]. A more promising approach has been to make a water-soluble biocide and trialkyltin methane- and ethanesulphonates have been shown to possess excellent activity when applied in aqueous solutions to wood substrates [111, 117]. Aqueous solutions of these alkylsulphonates can be prepared in distilled water with concentrations up to 3%. Although the presence of salts in the water can cause a reduction in aqueous solubility, a recent study [118] has shown that this is not likely to be a problem with the natural waters to be found for commercial use. Extensive testing has provided encouraging results [119]. A recent paper [120] examined the effects of tributyltin methanesulphonate and tributyltin *N,N*-dimethyldithiocarbamyl acetate on the deterioration of rubberwood stakes. The organotin preservatives were applied at ground level as well as above and below ground. Best results were obtained with the second compound. Recently, a new water-soluble fungicide, tributyltin mesylimide, has been described [121].

12.5.2 *Crop protection*

The importance of pesticides for crop protection can hardly be overestimated, since fungal or insect attack can cause widespread devastation with consequent serious food shortages, unless checked. A number of triorganotin compounds have been developed as agrochemicals and are successfully used today, in small, specialized applications, especially in the control of disease in potato and sugar beet crops. Work is continuing, both to develop new and more effective organotin pesticides and to design other ways of employing them in, for example, integrated campaigns with other agents such as chemosterilants. Safety/risk assessment of pesticides has been described [121]. The use of organotin compounds in agriculture has been reviewed by Crowe [122]. The first compounds to be introduced were triphenyltin acetate and triphenyltin hydroxide. Basic studies on the bioactive properties of organotin compounds had shown the high fungistatic activity of triphenyltins, which was accompanied by a low activity against plant life. A detailed review of triphenyltin compounds has been published [123], covering physical, chemical and biological properties, toxicology, analysis and environmental behaviour, as well as their use in agriculture. These triphenyltin compounds have proved successful in protecting crops against a variety of fungal diseases, including potato blight, leaf spot on celery, rice blast, coffee leaf rust and coffee berry disease. A product based on triphenyltin chloride has also been used in Japan to control leaf spot and leaf blight on sugar beet and late blight on potatoes.

The agricultural uses of organotins were further expanded with the discovery that certain compounds were effective miticides for use on fruit trees. The first compound to be introduced in 1968, was tricyclohexyltin hydroxide, but this was later withdrawn from use in most countries following adverse mutagenic test results in rabbits. Two other miticides have since been introduced successfully. These are bis(2-methyl-2-phenylpropyltin) oxide, commonly referred to as bis(trineophyltin) oxide or fenbutatin oxide [124] and 1-tricyclohexylstannyl-1,2,4-triazole, commonly known as azocyclotin [125], which was developed in Germany in 1980. These acaricides are highly selective and give excellent control of harmful arachnids such as the two-spotted spider mite, the European red mite and the Pacific spider mite, with little effect on other predatory mites and insects. The characteristics of these organotin pesticides have been described [126].

Organotin pesticides are applied as suspensions in water, made up from wettable powder. The timing and number of applications of the product are important and manufacturers' recommendations should be followed. The principal advantages of organotin agrochemicals (which possess mainly prophylactic action and do not exert systemic effects) are their low toxicity to the crop to be protected, lack of acquired resistance to these compounds by the pests, their effectiveness at low concentrations and the fact that they

break down under the effects of the environment into less toxic di- and mono-derivatives and eventually into harmless inorganic forms of tin, so that their use constitutes no long term pollution problem.

A very large body of research has been conducted into organotin agrochemicals and this is much concerned with improving the effectiveness of these compounds in known applications and with assessing their potential in new uses. The antifungal activity of tri-*n*-butyltin acetate against some common yam rot fungi has been investigated [127] and the antifungal activity of triphenyltin compounds has recently been studied [128]. One approach has been to introduce variations in the ligand groupings which are bio-active themselves [129]. Some organotin compounds exert an antifeedant effect, that is, they inhibit insects at the sensory level from feeding on treated products [130]. There is interest in this type of crop protection because it can be successfully integrated with other measures, such as trapping, sterilization or controlled use of insect predators [131]. Another approach which is being assessed is that of controlled release of pesticide, whereby the toxicant is incorporated into a polymeric matrix allowing a slow release from the surface, subjecting the target organism to chronic intoxication from small doses over a long period. Although interesting, this system has not to date been developed commercially with organotin pesticides.

12.5.3 *Antifouling coatings*

One established use of triorganotin compounds is in antifouling paints, although environmental concerns have somewhat restricted this application in recent times. Any surface which is immersed in water for any length of time becomes a target for attachment of aquatic organisms such as slime, bacteria, plant forms such as algae, or marine animals such as hydroids, crustaceans, molluscs and tunicates. On the hulls of vessels, such fouling can increase the weight and drag, leading to a greater consumption of fuel. It has been estimated that after 6 months in service, a vessel needs to expend 40% more fuel to maintain a normal cruising speed. One much-used solution has been to apply antifouling coatings, for example in the form of paints, to the hull. These antifouling paints then slowly release a toxicant which kills attached organisms and inhibits further attachment. Paint formulation has to be carefully controlled so that the toxicant is released at an effective level to kill the organisms, but slowly enough to provide long term protection.

In the early 1960s triorganotin compounds began to be used in such paints and their use soon grew to considerable proportions; this early work has been reviewed [132]. By 1991, about 80% of ships greater than 4000 dwt operating in world fleets were using a tributyltin-based antifouling system, tributyltin fluoride being commonly used as toxicant. Initially these paints were used to protect small yachts as well as large vessels. Concern about the environmental effects of antifouling paints has been expressed, particularly in areas

where there is a high density of small pleasure craft, coupled with poor water exchange. Current legislative controls for small boats in many parts of the world have proved to be effective, resulting in significant decreases in tributyltin levels in seawater and in the recovery of mariculture activities such as oyster rearing (tributyltin compounds had been shown to have a deleterious effect on the development of the Pacific oyster). The current position regarding organotin antifouling coatings and their use has been summarized by Karpel [134]. Most countries now ban the use of tributyltin compounds on boats of 25 m length or less; however, they are still used extensively on large tankers or naval craft where speed and operating efficiency are of prime importance. An important breakthrough in their effectiveness occurred with the introduction of so-called 'self-polishing' copolymer formulations [135]. In these systems the tributyltin moiety is part of an acrylic polymer and is slowly released under the action of flowing seawater at a uniform and linear rate. This not only means that no significant amounts of toxicant are released when the vessel is stationary, such as when it is in harbour, but also ensures that the hull remains smooth throughout the life of the coating since, as used paint is eroded away, a fresh layer is exposed. This self-polishing facility further adds to the operating efficiency of the vessel. Protection for up to 5 years can be achieved with these systems. These self-polishing systems accounted for 69% of the antifouling market in 1993 [136].

The fate of tributyltins in the aquatic environment has been the subject of study [137, 138] and environmental criteria have been established [139]. Although some short term effects may occur in localized areas, the bulk of evidence suggests that long term pollution is not likely to be a problem, since tributyltins tend to degrade to less toxic di- and monobutyltin forms in the environment. Proposals to monitor and control the worldwide usage of tributyltin-based paints have been supported by the chemical and marine paint industries [133]. Other organotin-based antifouling systems have been developed and are used to a limited extent. One approach has been to incorporate the organotin toxicant in an elastomeric matrix which is applied to the hull surface as a cladding. Organotin polysiloxanes have organotin moieties chemically bonded to a siloxane polymeric backbone [140]. Release of the toxicant takes place via hydrolysis of the tin-oxygen-silicon bond. Unlike organotin acrylate polymers which are typically linear, polysiloxanes exhibit three-dimensional crosslinking which provides a denser, more durable film.

12.5.4 Materials protection

Triorganotin compounds are also used to some extent to protect miscellaneous materials against biodeterioration under the influence of fungi, bacteria or algae. A review of the use of organotin compounds for biocidal protection has been published [141]. Formulations containing TBTO and a quaternary ammonium compound have been successfully used to protect

masonry and stonework against the attachment of mosses and lichens [142, 143]. Water-soluble organotin biocides also have some potential in this area [117].

Organotin biocides can be used to protect certain textile fabrics against insect attack and also against microorganisms causing rotting of fabric. Studies with triphenyltin compounds on wool [144] showed that the organotins did not adversely affect textile qualities and acted as a larvicide for the clothes moth and a pronounced antifeedant for the carpet beetle during a 14-day bioassay. An organotin-based formulation (TBTO plus hexachlorocyclohexane) is available for protecting old books, manuscripts, etc., from insecticidal and fungal attack. Combinations of TBTO or tributyltin benzoate with quaternary ammonium compounds have been used to prevent slime formation during paper making, counteracting not only bacteria but also fungi and algae [5]. Tributyltin benzoate has also been used in disinfectant formulations applied to hospital floors to prevent cross-infection and to sanitize some clothing, such as footwear.

12.6 Heterogeneous catalysts

In heterogeneous catalysis the function of the catalyst is to provide a suitable solid surface upon which the required reaction occurs and the reactants are commonly in the gaseous state. Tin(IV) oxide is used as a heterogeneous catalyst in a number of industrial processes, often in combination with a second oxide. This application has been reviewed [145]. Tin(IV) oxide alone is mildly oxidizing but by incorporating a second element, the catalyst can be 'tuned' to provide a wide range of activity and selectivity. Suitable elements include phosphorus, antimony, bismuth, vanadium, chromium, molybdenum, tungsten, manganese and copper. These catalysts can be used to promote the oxidation of carbon monoxide, sulphur dioxide and saturated and unsaturated hydrocarbons, as well as other organic compounds. They also catalyse the ammoxidation and isomerization of alkenes and the dehydration of alcohols. Harrison [146] has examined the chemical reactions occurring on the surface of tin(IV) oxide in these and other processes and their influence on the reactions. The method of preparation of the mixed oxides can have an influence on their catalytic activity and Wassel and coworkers [147, 148] have studied the influence of preparation method on the physicochemical and catalytic properties of tin-molybdenum catalysts.

Another group of tin-containing catalysts which have found industrial use are the tin-platinum and tin-rhenium systems, which are usually supported on alumina. These have been shown to be effective in the dehydrogenation, dehydrocyclization, cracking, isomerization and hydrogenation of hydrocarbons, reactions of importance in the petrochemical industry [149]. An interesting property of tin(IV) oxide-containing catalysts is the ability to

promote the low temperature oxidation of carbon monoxide by nitrogen oxides and oxygen. These reactions are of great importance in the removal of toxic gases from motor vehicle exhaust emissions. The catalytic systems currently favoured for this purpose consist of platinum or palladium metal dispersed over a ceramic honeycomb monolith support to which they are keyed by an oxide film such as alumina. One disadvantage of such systems is that low temperature catalytic activity is reduced in the presence of water vapour, frequently present in exhaust emissions. There is some evidence that improved performance can be obtained if tin(IV) oxide is used as the support [150, 151]. Not only is the catalytic activity at 60 °C greater than with an inert support, implying that tin(IV) oxide itself assists the catalytic process, but also the activity is enhanced by the presence of water vapour. These effects appear to be related to the promotion by water vapour of 'spillover' of activated carbon monoxide on to the tin(IV) oxide. Such a system has been successfully used in carbon dioxide gas lasers to regenerate carbon dioxide lost by dissociation into carbon monoxide and oxygen under the effect of the electrical discharge. Using this system, the power output of the laser can be maintained at room temperature [152]. Sermon *et al.* have studied the influence of weak chemisorption on the oxidation of carbon monoxide on tin(IV) oxide-supported platinum [153]. Russian workers have investigated effects of heat treatment of hydrated tin(IV) oxide, used as a support for a palladium catalyst, on the catalytic activity for oxidation of carbon monoxide [154]. This ability of tin(IV) oxide to oxidize carbon monoxide has also led to its use in air purification applications, for example in safety masks and in submarines.

12.7 Pharmaceuticals

Tin chemicals have a small but important use as pharmaceutical agents in the fields of dentistry, medicine and veterinary science, and research is continuing in these fields. A number of general reviews have been published [155–159].

12.7.1 Dentistry

It is a well known fact that fluoride is an important agent in preventing tooth caries. The fluoride either reacts with tooth enamel to reduce its susceptibility to dissolution in bacterial acids or interferes with the production of acid by bacteria within dental plaque. Multiple modes of action may account for the remarkable effectiveness of fluoride at low concentrations. Tin(II) fluoride has figured in a number of commercial toothpastes [160], as well as finding use in dentistry as a direct topical application to children's teeth. The American Dental Association has approved materials for topical application containing 1.23% acidulated phosphate fluoride, 2% sodium fluoride or 8%

tin(II) fluoride [161]. Tin(II) fluoride is approved at 0.4% in dentifrices. The effect of amine fluoride–tin(II) fluoride-containing toothpaste and mouth washes on dental plaque, gingivitis and plaque and enamel F^- accumulation has been studied [162]. Trials have also been conducted with a prophylactic paste based on tin(II) hexafluorozirconate which would, on application by a dentist, polish the teeth as well as reduce enamel solubility and decay.

Room temperature vulcanizing (RTV) silicones are used in dentistry and have several advantages for the production of dental prosthetic devices such as crowns, bridges and inlays [163]. These devices require a means of producing an accurate impression of the jaw, with or without teeth, as a preliminary to making a model. RTV silicones catalysed by tin chemicals, as described in section 12.2.2, have a shelf life of 2 years or more, have a setting reaction completely free from gas evolution, have a mild, pleasant odour and are non-tacky, being easily wiped away from unwanted areas during mixing and setting. Tin compounds used as catalysts in dental silicones include tin(II) octoate (cure time 0.5–2 min) and dialkyltin dilaurates (cure time 10–20 min) [164]. When dibutyltin dilaurate is employed, it also has the advantage that it inhibits the inter-oral growth of *Candida albicans* [165].

The use of tin(IV) oxide coatings, applied to alumina by vapour deposition techniques, to improve the bonding of dental restorations, has been investigated [166]. Significant improvements in bond strength were obtained in some cases.

12.7.2 Medical applications

Tin(II) salts are used in the preparation of radiopharmaceuticals, for example compounds labelled with the ^{99m}Tc isotope by reaction of the Tc^{4+} pertechnetate ion with a tin(II) compound, usually the chloride. These radiopharmaceuticals are widely used in diagnostic nuclear medicine for lung, bone and liver scintigraphy [167]. Hydrous tin(IV) oxide gels exhibit ion exchange properties and, unlike conventional organic exchange resins, they are stable above 150 °C and are resistant to strong acids and to nuclear radiation. This has made them suitable for use in chromatographic columns for separation of radionuclides required in medical techniques such as positron emission tomography [168]; the technique has also been used to isolate strontium radioisotopes from fission products [169]. The use of hydrated tin(IV) oxide to produce ^{82}Sr from metallic Rb targets has recently been reported [170].

A considerable body of research has been conducted into exploring the antitumour properties of certain organotin compounds [158, 171, 172]. One approach has been to model compounds on the *cis*-platin drugs currently in use. Diorganotin dihalide and dipseudohalide octahedral complexes with monodentate or bidentate ligands have exhibited reproducible activity against P388 lymphocytic leukaemia in mice. The activity is lower than that of *cis*-platin and its analogues, but toxic side-effects are much less. Di-*n*-

butyltin derivatives of substituted salicylic acids have given promising results *in vitro* against some human tumour cell lines and are the subject of a patent [173]. Further work is continuing to increase the water solubility of the diorganotin moiety, since this is thought to be a factor influencing the degree of effectiveness [174]. One promising use of inorganic tins is in the treatment of neonatal jaundice in newborn infants [175]. This condition, known as hyperbilirubinaemia, can produce harmful effects due to accumulation of the bile pigment, bilirubin, in the bloodstream. The use of tin protoporphyrin to prevent this condition has been proposed and trials in the USA have been reported as showing favourable results [176]. The potential of tin protoporphyrins has been examined in general terms [177]. One possibility is their use in a new photodynamic therapy for cancer. This therapy makes use of photosensitizing agents such as certain porphyrin derivatives which selectively accumulate in tumour tissue and which, on exposure to light, induce either plasma membrane or intracellular damage which leads in turn to destruction of the tumour. To date, encouraging results have been obtained in animal studies, using low doses of dichlorotin purpurins combined with red light [178]. Use of tin ethyl etiopurpurin as an alternative antifibrotic treatment following glaucoma surgery has been reported [179].

In the field of preventive medicine, tributyltin compounds have been tested as molluscicides for eliminating snail carriers of the parasitic blood flukes or schistosomes responsible for the debilitating illness known as bilharzia (or schistosomiasis). The aquatic snail acts as part of the life cycle of the parasite (eggs → free-swimming miracidial larvae → hatching of sporocysts in snail host → cercariae in water). Tests have been conducted using a slow release system comprising TBTO or other organotins impregnated into rubber pellets. These pellets float on waters frequented by host snails and release low, controlled doses of the toxicant, which are lethal to the snails but with minimal effect, at the used dosage, on other aquatic life. Organotins have also been tested in controlled release formulation for control of mosquito larvae [180]. Dioctyltin maleate at a dose level of 200 mg kg^{-1} has been tested against Leishmaniasis (a parasitic infection of the skin or viscera in humans, transmitted by small, blood-sucking sand flies) [181] and a series of organotin complexes of Schiff bases containing sulphur and fluorine have been tested *in vitro* for amoebicidal activity [182].

12.7.3 Veterinary applications

Certain organotins have found application in animal husbandry as anthelmintic agents in poultry and as insecticides for sheep and cattle. Dibutyltin dilaurate is one of the constituents of a commercial product for combating worm infections in turkeys and other poultry. Organotin acaricides have been tested against the mite causing scabies in sheep [183].

12.8 Fire prevention

In recent years the potential for tin-based fire retardants has greatly increased. Initially used to protect woolly sheepskins, the fire-retardant and smoke-suppressant properties of certain tin chemicals in synthetic polymers should lead to a large new market.

12.8.1 *Natural fibre treatments*

Two treatments were developed to protect woolly sheepskins: a spray treatment based on tin(II) chloride, ammonium hydrogenfluoride, isopropanol and polishing agents, and an immersion treatment employing K_2ZrF_6 , tin(II) chloride and hydrochloric acid [184]. These treatments offer advantages over those based on titanium or zirconium salts. Some work has also been conducted into the use of inorganic tin-based aqueous systems to impart flame resistance to cotton and other cellulosic materials [185].

12.8.2 *Additives for synthetic polymers*

The increasing use of plastics has changed the character of the fire problem, introducing hazards of smoke and toxic gases. There is a strong need for additives which, in addition to retarding the speed of flame, can also suppress the emission of smoke and toxic gases such as carbon monoxide. Work at the International Tin Research Institute (now ITRI Ltd) demonstrated the effectiveness of certain inorganic tin compounds as fire retardants in plastics and elastomers. Following preliminary studies, zinc hydroxystannate and zinc stannate were selected for more intensive study. Flammability of plastics samples was assessed by specialized techniques, including the limiting oxygen index (LOI) test, which measures the minimum oxygen content needed to support combustion of a test specimen in an upward flowing mixture of nitrogen and oxygen; a high LOI value indicates flame retardancy. Smoke density measurements have been conducted using an NBS smoke box. The cone calorimeter test, which measures the rate of heat release and visible smoke from burning materials, is considered to provide the data most relevant to actual experience [186]. This development work has been reviewed [187]. Data have been gathered, showing the effectiveness of zinc hydroxystannate and zinc stannate as flame retardants and smoke inhibitors in PVC (rigid and flexible forms), polychloroprene, alkyd resin-based paints, thermoplastic/elastomer compositions where the halogen is incorporated as a supplementary additive, in halogenated polyester resins and in chlorosulphonated polyethylene [188–190]. A marked degree of flame retardant synergism is observed when the tin compounds are used in conjunction with additive-type halogen derivatives such as chlorinated paraffin wax [191]. Zinc hydroxystannate and zinc stannate have been shown to be very effective

flame retardants in alkyd resin-based gloss paints which contain titanium dioxide pigment and chlorowax as the halogen source. Encouraging results have also been obtained in halogen-free polymers which are finding increasing use, particularly in underground transport and in mining and electrical installations where emission of smoke and corrosive gases must be minimized at all cost. At relatively low incorporation levels (below 10 phr), zinc hydroxystannate has been shown to increase significantly the flame retardancy of alumina trihydrate-filled natural and synthetic rubber compositions, provided a sufficient level of inorganic filler is present.

The tin compounds have the advantage of being non-toxic, safe and easy to handle. There may also be potential for tin-based fire retardants as replacements for organophosphorus-based flame retardants where some environmental concern is being expressed, for example in rigid polyurethane foams. Zinc hydroxystannate and zinc stannate are currently being marketed as proprietary formulations. Although there is little difference in general between the effectiveness of zinc hydroxystannate and zinc stannate, the latter compound is the preferred additive for high temperature processing polymers, since zinc hydroxystannate undergoes thermal dehydration at temperatures above about 180 °C. Future advances are likely to involve the development and subsequent introduction of improved grades of these compounds, including ultrafine powders (0.1–0.4 μm particle size), colloidal dispersions and coated additives. Ultrafine material does not separate out in polymer resins and can be used in formulations where translucency is required. The fire retardant efficiency is also markedly raised over that of the standard product, as shown in Figure 12.5 (p. 472).

12.9 Miscellaneous uses

Tin chemicals have a wide range of other uses and although some of these are quite small in tonnage terms, others have potential for considerable growth.

12.9.1 *Semiconducting applications*

Tin(IV) oxide is a semiconductor and this property has been exploited in a number of devices and technologies. One growing use is in gas sensors which can detect and monitor the presence of hazardous gases [192, 193]. In fact, tin(IV) oxide is the most widely used material for the construction of semiconductor gas sensors and has remained at the forefront of the technology for more than two decades. Tin(IV) oxide is a non-stoichiometric oxygen-deficient compound showing typical n-type semiconductor behaviour. In an oxygen-containing atmosphere, oxygen species are chemisorbed on to its surface by withdrawing electrons from the conduction band of the solid; this raises the electrical resistance. At temperatures in the range 200–500 °C, the

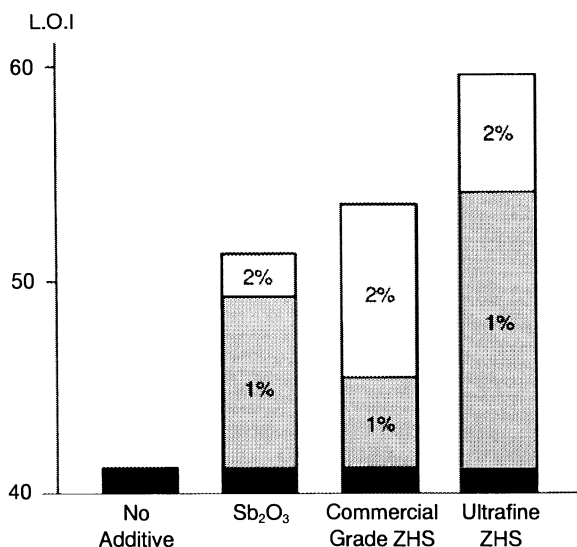


Figure 12.5 Flammability (LOI) data for brominated polyester resin samples, highlighting the exceptional performance of ultrafine ZHS (ITRI Ltd).

presence of reducing (or other) gases can chemically remove a part of the oxygen, releasing the bound electrons back into the conduction band, thus raising the conductivity. These changes in electrical resistance can be made to trigger a signal, indicating the presence of such gases. The increase in conductivity can also be a measure of the gas concentration. Sensors are available for the detection of carbon monoxide and also for hydrocarbons, other combustible gases, alcohol, ammonia, etc. The tin(IV) oxide may be used in the form of a porous sintered material or as a thin (100 nm) layer on a flat ceramic substrate.

A considerable body of research is in progress to improve the performance of tin(IV) oxide-based systems. Harrison [146] looked at the effect of surface reactions occurring on tin(IV) oxide, on the gas sensing properties. Gaggiotti *et al.* [194] also examined the surface chemistry of tin(IV) oxide-based gas sensors. Song [195] studied factors influencing the carbon monoxide-sensing properties of tin(IV) oxide calcined at different temperatures. A relatively high sensitivity was obtained in a low gas concentration with a largely crystallized sample. Techniques for increasing the selectivity of commercially available tin(IV) oxide-based sensors for monitoring combustible gases in process environments have been described [196]. The use of tin(IV) oxide–zirconium oxide thin films for detecting phosphine in air is the subject of another paper [197]. One way of improving the selectivity and response of a tin(IV) oxide sensor is by incorporating various additives. Thus the catalytically active elements palladium and platinum can greatly enhance sensitivity to reducing

gases [198, 199]. The primary advantage of tin(IV) oxide-based detectors is that they are low in cost. These types of sensor are used extensively in Japan, where the Figaro Engineering Company of Japan is currently producing some 14 million such sensors each year.

Tin(IV) oxide layers 1 μm thick, doped with fluorides, figure in photovoltaic panels comprising a thin layer (0.5 μm) of silicon semiconductor sandwiched between two electrodes [200, 201]. The back electrode is vacuum-deposited aluminium, whilst the front electrode, facing the light source, is a transparent layer of tin(IV) oxide, possessing a suitably high conductivity. These low cost photovoltaic systems have been used in a major power generating installation in the USA. More recently, it has been reported [202] that a similar system is to be used to generate solar energy at half the current cost. The solar panel has three amorphous silicon alloy layers, each of which converts a different region of the spectrum of sunlight into electricity. An indium–tin oxide film is deposited over these layers as an antireflective coating. Tin(IV) selenide is a semiconductor with an energy band gap of about 1 eV and has been considered as a potential material for photovoltaic applications [203]. Films have been grown by the hot wall epitaxy technique on glass, mica and potassium chloride substrates; electrical resistivity, Hall mobility and optical absorption have been measured.

12.9.2 *Colouring of aluminium*

Tin-based electrolytes have been used to colour aluminium for use in architecture [204]. First a normal unsealed anodized coating is produced, consisting of an adherent transparent oxide film. Small metal particles are deposited at the base of the pores by immersion in a metal salt solution with passage of an alternating current. These metal particles scatter the incident light and can produce a range of colours from light bronze to black, the colour being dependent on the amount of metal deposited and not on the oxide film thickness. Tin, cobalt and nickel electrolytes are used in this process, but tin-based processes have less limitations. Typical conditions and procedures for operating tin-based colouring processes have been described [205]. The electrolyte is often tin(II) sulphate but other tin electrolytes have been used; an antioxidant is often present to prevent the formation of insoluble tin(IV) salts and the solution has a pH of about 1. Two new processes are being developed to widen the possible colour range which can be obtained. In a combined electrolytic/absorption method [206], an anodized sample is first electrolytically coloured to a mid or light bronze; this is followed by adsorption dyeing using an organic dye after which the coating is sealed. Although expensive to operate, the process is claimed to produce weather-resistant golds, reds, blues, yellows and turquoise. A second approach is to control carefully the deposition process in order to produce optical interference effects [207]. The metal particles deposited in the pores of the film are induced

to assume a rod-like form by enlarging the pores. Enlargement is achieved using a second anodizing treatment in phosphoric acid with an AC field. The electrolytic colouring step then follows, plus a further special treatment to develop the desired colour. Although still at the developmental stage, this process has been shown to be capable of producing blue, green, red and yellow interference colours in anodic films [208].

12.9.3 *Water repellents*

Water repellent properties have been exhibited by certain monoalkyltin compounds and these have been tested on building materials (limestone, bricks and concrete) [209] and on cellulosic substrates (cotton, paper and wood) [210]. Octyltin trilaurate has been shown to impart a water repellency to limestone comparable to that shown by a commercial silicone treatment. Other compounds, such as octyltin and dodecyltin trichlorides, show potential as dampproofing treatments for bricks. When assessed on cotton fabrics in the British Standard 3702 Vertical Spray Test, sodium butanestannoate, butylchlorotin dihydroxide, *n*-octylchlorotin dihydroxide and butyltris-(triphenylsilanoxy)tin all imparted water repellency to the fabric [184].

12.9.4 *Reducing agents*

The strongly reducing properties of the tin(II) cation find application in reagents for preparative organic and inorganic chemistry [211]. Reactions of industrial significance include the reduction of nitriles or acid anilides to the corresponding aldehyde, reduction of the olefinic linkage in unsaturated carbonyl compounds to form the corresponding substituted monoalkyltin trichloride, and reduction of nitro groups to amines [3].

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13 Solid state NMR spectroscopy of tin compounds

TERENCE N. MITCHELL

13.1 Introduction

Virtually all preparative chemistry is carried out in solution, and studies on reaction mechanisms can only be carried out easily in homogeneous media. However, with very few exceptions exact information on the spatial structures of molecules can only be obtained by subjecting them to single crystal X-ray diffraction procedures. These can of course only be applied when suitable single crystals are available, and this is in general not the case. The structural information thus obtained is generally correlated with spectroscopic information obtained in the gas phase (mass spectrometry) or in the liquid phase (NMR spectroscopy).

The latter is the tool most widely used for measurements in solution because of the plethora of useful information which it can provide. Up until a few years ago, solid state NMR was a tool used rarely by chemists (or at least by organic and inorganic chemists), since methods for obtaining high resolution spectra had not been developed. Although these now exist and will be described briefly below, even today there is no procedure available for obtaining high resolution solid state proton NMR spectra. The results obtained using the CRAMPS technique (combined rotation and multiple pulse spectroscopy) are comparable at the best with those obtained on 40 Hz spectrometers in the early days of NMR.

The situation is however completely different when we turn to ^{13}C and other heteronuclei, including ^{117}Sn and ^{119}Sn (as in the liquid state, both tin nuclei can be used and indeed have similar nuclear properties, but ^{119}Sn is generally preferred). Linewidths can be of the order of 10–100 Hz or even less (as in the case of carbon ^{13}C spectra of plastic crystals) rather than the many tens of kilohertz familiar from 'traditional' solid state NMR. It thus becomes possible to determine not only chemical shifts but in many cases spin–spin coupling constants involving tin or other heteronuclei present in the molecule. In addition, the material under study simply has to be solid in nature: either crystalline or amorphous, either monomeric, oligomeric or polymeric.

Thus high resolution solid state NMR spectroscopy can provide an invaluable 'bridge' between the structural data obtained on a single crystal and the NMR spectroscopic data obtained in solution. With the help of this bridge it is possible to make clear statements about the structure of the

compound in the solid state and in solution, and thus to develop better models for understanding the mechanisms involved in reactions carried out in the liquid state.

Which advances have opened this new door to the chemist? The reader who is interested in a detailed historical survey of the development of the technique is referred to the 'bible' of solid state NMR, the monograph written by Colin Fyfe a number of years ago [1]. For those (no doubt the majority) who are interested in results and how to obtain them easily and accurately, a brief and by no means stringent treatment of the instrumental techniques will follow.

A combination of three different techniques is normally used: CP, HPD and MAS. CP stands for 'cross-polarization', i.e. magnetization transfer from an abundant source (normally the proton) to the nucleus under consideration. Such techniques are used routinely in liquid state NMR today; INEPT and DEPT were two early examples. Cross-polarization can become difficult at high spinning speeds (see below) and is of course often not possible when inorganic tin compounds are under study, simply because no protons are available. Nevertheless, measurements on inorganic tin compounds have also been made, and these will be referred to below.

HPD refers to the 'high power proton decoupling' which is required when dealing with solids. MAS is 'magic angle spinning', a technique which merits a few words of explanation, based on the differences in the physics of NMR in the liquid and solid states. In a liquid the molecules are subject to rapid movement but in the solid state this motion is greatly restricted. Thus the strong dipolar interactions, which are motionally averaged to zero in the liquid, are dominant in the solid state; the presence of quadrupolar nuclei also makes itself felt much more for solid samples. The chemical shift, which is in fact a tensor quantity, is also averaged in solution, so that only the isotropic chemical shift can be extracted from conventional spectra. While in the liquid we observe the average of the three orthogonal principal components, the solid state spectrum may consist of only a single line but more often consists of a family of lines, which (in principle) contain the information necessary for the extraction of the three principal components. The factor which plays a dominant role in determining the form of the spectrum is the chemical shift itself, which is very often anisotropic, i.e. the values of the three principal components are unequal; in the case of tin the differences can be of the order of hundreds of ppm! The higher the anisotropy, the more lines there will be in the spectrum. This chemical shift anisotropy (generally referred to as CSA) is in addition field dependent, which will have important consequences as we shall see.

The technique of magic angle spinning is based on the fact that the equation which expresses the dipolar interactions has a term $(3\cos^2\Theta - 1)$. This term is thus equal to zero when $\Theta = 54.7^\circ$. When the sample is aligned at an angle of 54.7° to the external magnetic field B_0 , the dipolar interactions are

therefore zero. The sample is also spun, not at about 20 Hz as for liquids, but at several kilohertz. Until recently spinning speeds of around 5 kHz were normal using sample rotors of 7 mm external diameter, generally made of zirconia. Now it is possible to use rotors (all of which are expensive as they must be very accurately machined, and there are only three suppliers) of only 4 mm external diameter, and these permit the use of rotation frequencies of 15 kHz and above. In the case where the chemical shift anisotropy is not equal to zero, the spectrum will contain not only a band (the centre band) at a position corresponding to the isotropic chemical shift (the value determined in solution), but also a series of spinning sidebands separated by the rotational frequency of the sample. (These sidebands contain the information required for obtaining the principal components of the chemical shift tensor, which are, however, normally not required by the chemist who is interested only in simple structural aspects.)

Since the chemical shift anisotropy is field dependent, the number and magnitude of the spinning sidebands is also field dependent; indeed, the centre band is often by no means the strongest band in the spectrum! This basically requires that the spectroscopist should search for a compromise: if a high magnetic field is used there will be a signal intensity advantage but also a large number of spinning sidebands, while a lower field gives a simpler spectrum but at the cost of a reduced intensity. The best compromise is probably to use a spectrometer which operates at 200–250 MHz for protons. The intensity of the spinning sidebands is reduced when the spinning speed is increased, but for samples with a high CSA they cannot be suppressed completely, particularly as high spinning speeds bring new problems, such as the inefficiency of cross-polarization.

How does one go about finding the centre band when it is surrounded by spinning sidebands? One possibility is to use a pulse technique known as TOSS (total suppression of spinning sidebands), but this sequence must be carefully set up in order for it to function correctly and its application may bring new problems, in particular since its theoretical basis is still subject to discussion. The simpler (and more primitive) technique is to record the spectrum twice using different spinning rates: only the centre band will remain in the same position in both spectra.

As we shall see below, solid state tin NMR is a technique which has so far been used by relatively few research groups working in the organotin field. This may well be due to the fact that it still appears to many to be a very difficult technique which can be successfully practised only by 'experts'. Such fears are no longer justified today: spectrometer manufacturers can supply a 'solids package' suitable for use in either a wide bore or a narrow bore magnet. The magic angle is now set automatically, and the only real difficulty often lies in packing the sample into the sample container, since non-uniform packing prevents the achievement of the high spinning speeds required.

13.2 The early period (1978–1985)

The pioneering publication in this area appeared as early as 1978, when Lippmaa *et al.* [2] applied solid state NMR techniques to ^{13}C , ^{29}Si and ^{119}Sn . Although only two organotin compounds were studied, one of these was by chance a very important one: tetracyclohexyltin is now the accepted secondary standard ($\delta = -97.35$). The next publications concerned with ^{119}Sn did not appear until 1985: Harris *et al.* (then in Norwich) reported the spectra of tributyltin fluoride [3] and of trimethyltin hydroxide [4]. The majority of the work done on solid state tin NMR has indeed come from this group, now situated in Durham.

At this early stage commercial samples were analysed, and the interpretation of the spectrum of the trimethyltin hydroxide was later subjected to a reappraisal [5], as it turned out that the compound purchased contained about 50% of an 'impurity' in the form of dimethyltin oxide! In view of the high prices charged for organotin compounds this should of course never have happened, but even today it is not always advisable to accept purchased chemicals at their face value! In 1985 the present author spent some time in Durham learning the 'basics' of solid state NMR. At that time the 'state-of-the-art' spectrometer was a Bruker CXP-200 and it was necessary to set the magic angle 'by hand' using KBr added to the sample. The double-bearing rotor, which makes life much easier today, had not yet been introduced. However, we were able to observe tin–tin scalar coupling for the first time [6] because of the favourable linewidths encountered.

In the same year, Lockhart *et al.* [7] carried out the first systematic ^{13}C study of methyltin compounds and presented an empirical equation relating the one-bond tin–carbon coupling constant and the angle carbon–tin–carbon:

$$|{}^1J({}^{119}\text{Sn}, {}^{13}\text{C})| = 11.4(\theta) - 875 \quad (r = 0.995, n = 9) \quad (13.1)$$

Thus in 1985 the groundwork had apparently been done, and the advances in instrumentation which followed shortly afterwards (the double-bearing rotor, the availability of 'solid state upgrades' also for narrow bore magnets, and improvements in computing power) made it seem likely that solid state NMR would take its place as at least a semi-routine tool for the organic and inorganic chemists involved in tin chemistry. This has not in fact been the case, as can be seen by the number of papers referred to in this survey.

Perhaps this chapter will provide the necessary stimulus for the expansion of this potentially important technique by collating the data presently available.

The discussion will be continued not chronologically but by substance type, whereby a large heterogeneous group of papers will be gathered together under the term 'miscellaneous compounds' (which no author involved should consider as a pejorative term!).

13.3 Compounds with four tin–carbon bonds (Table 13.1)

Not unexpectedly, few compounds of this type have been studied, as a large majority of them are liquids and also because no great structural change can be expected on going from solution to the solid state or vice versa.

Tetraphenyltin has been studied twice [8,9], *c*-Hex₄Sn three times [2, 10, 11], in both cases with similar results. As mentioned above, the value of -97.35 for *c*-Hex₄Sn is now taken as the secondary standard value. This compound is commercially available and stable, gives a strong FID after a single transient and a linewidth of 14 Hz at 74.58 MHz. The shift differences between the solution and solid states for the three compounds Ph₃SnR (R = Me, Et, Bu) are relatively large, about 15 ppm, while for (PhCH₂)₂Sn(C≡CPh)₂ [12] it reaches about 30 ppm. These are likely to be effects caused by crystal packing.

Triphenylallyltin [10] exhibits two resonances because crystal effects lead to the presence of two non-equivalent tin sites in the asymmetric unit; this phenomenon is a common one in solid state NMR. An unusual spirocyclic tin compound has also been investigated [13].

13.4 Organotin halides (Table 13.2)

Trialkyltin fluorides are almost insoluble in organic solvents as they form coordination polymers with an F–Sn–F linkage. Thus the tin signal shows three centrebands which can be of very different intensities. δ_{iso} for each centreband is given separately in the table as reported by Harris *et al.* [14]

Table 13.1 Compounds containing tin–carbon bonds

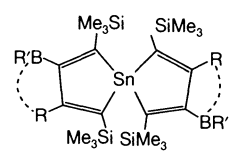
Structure	δ_{iso}	δ_{liquid}	Ref.
Ph ₄ Sn	-120.75	120 ± 10	8
Ph ₄ Sn	-117	137	9
<i>c</i> -Hex ₄ Sn	-92		2
<i>c</i> -Hex ₄ Sn	-97.35	94.2	10
<i>c</i> -Hex ₄ Sn	-92	94.2	11
Ph ₃ SnMe	-78	-93	11
Ph ₃ SnEt	-81	-98	11
Ph ₃ SnBu	-97	-111	11
Ph ₃ SnCH ₂ CH=CH ₂	$-117.3, -135.2$	120.4	10
Me ₃ SnC≡CSnMe ₃	-86.0		53
(Me ₃ Sn) ₄ C	48.2 ($^2J(\text{Sn}, \text{Sn})$ 328 ± 8)	49.8	6
(PhCH ₂) ₂ Sn(C≡CPh) ₂	-146	-175.3	12
	190.5	190.5	13

Table 13.2 Organotin halides $R_n\text{SnX}_{4-n}$

R	n	X	δ_{iso}	δ_{liquid}	Ref.
Bu	3	F			3
Me	3	F	41.5/24.1/6.7 $^1J(\text{Sn-F})$ 1.3 kHz		14, 15
Bu ^l	3	F	3.8/-13.1/-30.0 $^1J(\text{Sn-F})$ 1.26 kHz		14, 15
Ph	3	F	-198.1/-211.9/-225.6 $^1J(\text{Sn-F})$ 1.53 kHz		14, 15
Mesityl	3	F	-72.1/-82.0/-92.3 $^1J(\text{Sn-F})$ 2256 kHz -60.3/-70.4/-80.9 $^1J(\text{Sn-F})$ 2300 kHz		14, 15
Ph	3	Cl	-33/-35	-44.7 ^a	12
Ph	3	Cl	-19/-38 (1:3.6)	-48	9
PhCH ₂	3	Cl	105	52.5 ^a	12
Hex ^c	3	Cl	82	66.2 ^b	12
Hex ^c	3	Br	94	79.2 ^a	12
PhCH ₂	2	Cl	55	36.4 ^c	12
Me	2	Cl	74.5	137.0 ^c	12
Et	2	Cl	82	121.0 ^c	12
Et	2	Cl	79/95 (1:1.5)	126 ^c	9
Bu	2	Cl	84.0	123.4 ^c	12
Bu	2	Cl	280	121.8 ^a	2
Hex ^c	2	Cl	7.0	73.8 ^a	12
Me	2	Br	90.0	70.7 ^a	12
Hex ^c	2	Br	82.0	70.7 ^a	12
MeCO ₂ (CH ₂) ₃	1	Cl	-80.4	-38 ^d	18
MeCO ₂ (CH ₂) ₄	1	Cl	-168	-47 ^d	18
MeCO ₂ (CH ₂) ₅	1	Cl	-168	-67 ^d	18

^aIn chloroform.^bIn benzene.^cIn methylene chloride.^dIn deuteriochloroform.

who provide a detailed explanation of the effects involved in determining the nature of the AX_2 spin systems involved [15]. The coupling between tin and fluorine is large (1.3–2.3 kHz). Two non-equivalent tin crystal sites are present in the case of trimesityltin fluoride.

Organotin chlorides can also show the effect of the tin-(quadrupolar) chlorine interaction but this is relatively weak; a discussion is given in Ref. 16 and a full theoretical treatment in Ref. 17. Triphenyltin chloride and diethyltin dichloride again contain two non-equivalent tin sites, but the relative intensity values reported [9] are of doubtful value in any quantitative sense.

The difference between solution and solid state chemical shift varies from about 10 to as much as 70 ppm (the solid state value for Bu_2SnCl_2 [2] is almost certainly incorrect). While a quantitative discussion of this 'difference parameter' is difficult, particularly since crystal packing effects will be involved, it is obviously diagnostic of certain structural differences between the two states.

A very recent paper [18] deals with the coordination behaviour of compounds $\text{MeOCO}(\text{CH}_2)_n\text{SnCl}_3$ ($n=3-5$); solid state NMR is used as only one of a number of techniques. The solid state tin shifts make it clear that the behaviour is different for $n=3$ on one hand and $n=4, 5$ on the other. Both intra- and intermolecular interactions occur, and for $n=3$ an intramolecular alkoxy oxygen–tin coordination is suggested, while for $n=4, 5$ coordination is intermolecular.

13.5 Compounds with tin–oxygen bonds (Table 13.3)

Trimethyltin hydroxide [4, 5] and dialkyltin oxides [9, 19] are polymeric and thus insoluble in organic solvents. Thus no comparison between liquid and solid states can be made. Tricyclohexyltin hydroxide appears to be present as a monomer in chloroform solution but as a coordination polymer in the solid state [12]; a ^{13}C study could help in documenting this completely. Bis(trimethyltin) carbonate contains four- and five-coordinated tin sites [20, 21]

Table 13.3 Compounds with tin–oxygen bonds

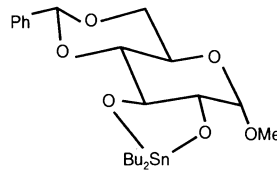
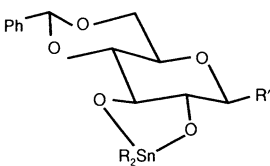
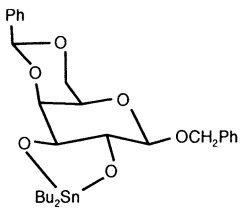
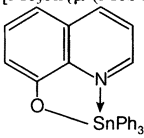
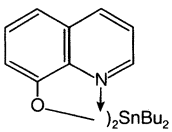
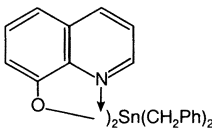
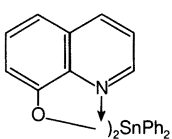
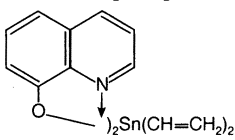
Compound	δ_{iso}	δ_{liquid}	Ref.
Me_3SnOH	−99		4, 5
Hex_5SnOH	−217	11.6 ^a	12
Me_2SnO	−152		4, 5, 19
Bu_2SnO	−173		9
Bu_2SnO	−177		19
$(\text{Ph}_3\text{Sn})_2\text{O}$	−75.2, −80.5 [$^2J(\text{Sn}–\text{Sn})$ 421]	−85.5 [$^2J(\text{Sn}–\text{Sn})$ 437.0] ^a	20
$(\text{Ph}_3\text{Sn})_2\text{O}$	−76.3, −81.7 [$^2J(\text{Sn}–\text{Sn})$ 421]	−85.0 [$^2J(\text{Sn}–\text{Sn})$ 437.0]	58
$(\text{Neophyl}_3\text{Sn})_2\text{O}$	56.0	57.7 [$^2J(\text{Sn}–\text{Sn})$ 558]	58
$(\text{Bu}_t^1\text{Sn})_2\text{O}$	−39.1 [$^2J(\text{Sn}–\text{Sn})$ 932]	−85.5 [$^2J(\text{Sn}–\text{Sn})$ 910]	58
$(\text{Bz}_3\text{Sn})_2\text{O}$	11.1 [$^2J(\text{Sn}–\text{Sn})$ 991]	9.2 [$^2J(\text{Sn}–\text{Sn})$ 664]	58
$\{[(2\text{-MeBz})_3\text{Sn}]_2\text{O}\}$	6.5 [$^2J(\text{Sn}–\text{Sn})$ 895]	22.5 [$^2J(\text{Sn}–\text{Sn})$ 721]	58
Me_3SnOAc	−27.2		20, 54
Bu_2SnOAc	−48/−54		9
$(\text{Me}_3\text{Sn})_2\text{CO}_3$	133.5, −62.0		20
$(\text{Me}_3\text{Sn})_2\text{CO}_3$	123.5, −62.2		21
$(\text{Bu}_t^1\text{Sn})_2\text{CO}_3$	86.5, 675.1, −96.4	101.7	21
$\text{Bu}_2\text{SnOCH}_2\text{CH}_2\text{O}$	−230	−189	8
$\text{Bu}_2\text{SnOCH}_2\text{CH}_2\text{O}$	−231 (polymer)		23
$\text{Bu}_2\text{SnOCHMeCHMeO}$	−205 (polymer)		23
$\text{Bu}_2\text{SnOCH}_2\text{CH}_2\text{O}$	−222, −224, −225, −226 (dimer mixture)		23
$\text{Bu}_2\text{SnOCH}_2\text{CH}_2\text{CH}_2\text{O}$	−278.5, 281.6 (polymer)		23
	−126.8, −128.6 (dimer)		23

Table 13.3 (*Contd*)

Compound	δ_{iso}	δ_{liquid}	Ref.
			
as above, R = Bu, R' = PhCH ₂	-128 (dimer)		23
as above, R = Bu', R' = Me	-213.0, -225.7 (dimer)		23
as above, R = Bu, R' = Me	-119, -127, -223, -234 (pentamer)		23
	-141 (dimer)		23
Me ₂ SnSCH ₂ CH ₂ O	-51	-21	22
Me ₂ SnSCH ₂ CH ₂ O	-31	-34	22
Bu ₂ SnSCH ₂ CH ₂ O	-41	-34	22
-(Oct ₂ SnO ₂ CCH=CHCO ₂)- _n	-295		9
[(Pr ⁿ Sn) ₁₂ O ₁₄ (OH) ₆] ²⁺	-310, -488		26
[Me ₃ Sn{μ-(MeSO ₂) ₂ N}Me ₃ Sn(μ-OH)] _n	94.8, 68.6		54
	-213.2 ¹⁴ N: -212.1/-215.2/-218.3	-190.1 ¹⁴ N: -192.5	17
	-277.4	-260.0	17
	-394.2	-335.2	17
	-417.2	-394.2	17
	-402.8	-394.1	17

^aIn chloroform.

while triisobutyltin carbonate contains a total of four sites of which three are observed (in the intensity ratio of 2:1:1).

Simple dioxastannolanes [8] and oxathiastannolanes [22] derived from ethylene glycol and its monothio analogue have been suggested to have the same structure in the liquid and solid states.

More complex dioxastannolanes derived from sugars as well as some simple dioxastannolanes and a dioxastannane have been studied in a very detailed paper by Grindley *et al.* [23]. The nature of the species present in the solid state and in solution is discussed and the reader is referred to this discussion.

Several internally coordinated compounds have been studied [24, 25] and exhibit the expected high-field resonances in both states. In the solid state, bands are split due to scalar and dipolar coupling with ^{14}N ; this was shown particularly clearly when an isotopomerically pure sample was used.

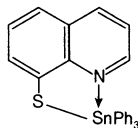
The hydrolysis of monoorganotin trihalides is a complex process and a cationic tin cluster has been obtained which contains six octahedral and six square-pyramidal tin sites [26].

13.6 Compounds with Sn–S, Sn–Se and Sn–Te bonds (Table 13.4)

The four-coordinate sulphides, selenides [27, 28] and tellurides [28, 29] investigated do not change their structure when dissolved but have two non-equivalent tin sites in the crystal. Tin–tin, tin–selenium and tin–tellurium coupling constants have been determined and appear to vary little between the two states [27, 28]. The use of a rotation-synchronized CPMG sequence for resolution enhancement has been suggested and described [27].

Table 13.4 Compounds with Sn–S, Sn–Se and Sn–Te bonds

Compound	δ_{iso}	δ_{liquid}	Ref.
$(\text{Me}_2\text{SnS})_3$	125.2, 107.7/ $J(\text{Sn-Sn})$ 193	131/ $J(\text{Sn-Sn})$ 195 ^a	27
$(\text{Me}_2\text{SnS})_3$	125.2	131.0/ $J(\text{Sn-Sn})$ 194 ^a	58
$(\text{Me}_2\text{SnS})_3$	I 125.6/ $J(\text{Sn-Sn})$ 198 \pm 2 (I–II)	131.6/ $J(\text{Sn-Sn})$ 205	28
Tetragonal	II 108.3/ $J(\text{Sn-Sn})$ 161 \pm 4 (II–II)		
$(\text{Me}_2\text{SnS})_3$	I 116.8/ $J(\text{Sn-Sn})$ 179 \pm 2 (I–II)		28
Monoclinic	II 111.5/ $J(\text{Sn-Sn})$ 195 \pm 4 (II–III)		
	III 102.4/ $J(\text{Sn-Sn})$ 190 \pm 2 (I–III)		
$(\text{Ph}_2\text{SnS})_3$	28.2, 19.0/ $J(\text{Sn-Sn})$ 197	17.8/ $J(\text{Sn-Sn})$ 208 ^a	27
$(\text{Bu}_2^i\text{SnS})_2$	119.4, 117.3	124.1/ $J(\text{Sn-Sn})$ 113 ^b	27
$(\text{Bu}_2^i\text{SnS})_2$	116.2	124/ $J(\text{Sn-Sn})$ 114 ^b	27
$(\text{Hex}_2^i\text{Sn})_2\text{S}$	26.6, 4.1/ $J(\text{Sn-Sn})$ 249	21.0/ $J(\text{Sn-Sn})$ 220.6 ^b	27
$(\text{Ph}_3\text{Sn})_2\text{S}$	–50.0, –53.2	–51.7/ $J(\text{Sn-Sn})$ 223	58

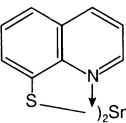
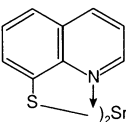
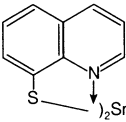
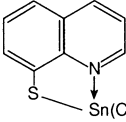
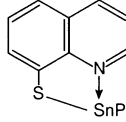
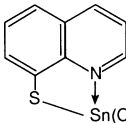
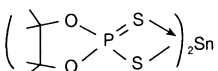


–147.0

–150.5

24

Table 13.4 (*Contd*)

Compound	δ_{iso}	δ_{liquid}	Ref.
 $\text{S} \rightarrow \text{Sn}(\text{CH}_2\text{Ph})_2$	-255.9	-235.2	24
 $\text{S} \rightarrow \text{SnPh}_2$	-274.4	-273.6	24
 $\text{S} \rightarrow \text{Sn}(\text{CH}=\text{CH}_2)_2$	-303.6	-282.4	24
 $\text{S} \rightarrow \text{Sn}(\text{CH}_2\text{Ph})_2\text{Cl}$	-145	-151.0	25
 $\text{S} \rightarrow \text{SnPh}_2\text{Cl}$	-186	-197.1	25
 $\text{S} \rightarrow \text{Sn}(\text{CH}=\text{CH}_2)_2\text{Cl}$	-210	-201.3	25
$\text{PhSn}(\text{S}_2\text{CNEt}_2)_3$	no signal after 48 h	-807 (coord. no. 7)	30
$\text{PhSn}(\text{S}_2\text{CNEt}_2)_2\text{Cl}$	-643	-649.9 (coord. no. 6)	30
$\text{Ph}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	-516	-502 (coord. no. 6)	30
$\text{Ph}_3\text{Sn}(\text{S}_2\text{CNEt}_2)\text{Cl}$	-311	-325/-340 (coord. no. 5)	30
$\text{Ph}_3\text{SnS}_2\text{CNEt}_2$	-165	-192 (coord. no. 4)	30
$\text{Ph}_3\text{SnS}_2\text{P}(\text{OEt})_2$	-53	-82	34
$(\text{Me}_2\text{SnSe})_3$	32.6, 21.1/ ^f $J(\text{Sn-Sn})$ 202 ^l $J(\text{Sn-Se})$ 1191, 1264	40.2/ ^f $J(\text{Sn-Sn})$ 254.3 ^a	27
$(\text{Me}_2\text{SnSe})_3$ (tetrag.)	21.9/ ^l $J(\text{Sn-Se})$ 1246 33.2/ ^l $J(\text{Sn-Se})$ 1180, 1132	46.6/ ^l $J(\text{Sn-Se})$ 1219 ^c	28
$(\text{Me}_2\text{SnSe})_3$	32.6/ ^f $J(\text{Sn-Sn})$ 202	42.0/ ^f $J(\text{Sn-Sn})$ 237	58
$(\text{Me}_2\text{SnTe})_3$ (tetrag.)	-178.6/ ^l $J(\text{Sn-Te})$ 2967, 3173 -227.8/ ^l $J(\text{Sn-Te})$ 3034	-196.2/ ^l $J(\text{Sn-Te})$ 3103	28
$[(\text{Me}_3\text{SiCH}_2)_2\text{SnTe}]_3$	-185/ ^l $J(\text{Sn-Te})$ 3150, 3238 -183.4/ ^l $J(\text{Sn-Te})$ 3089, 3158 -233.6/ ^l $J(\text{Sn-Te})$ 3043, 3190		29
 $(\text{P}=\text{S})_2\text{Sn}$	-257.1	-209.7	45

^aIn benzene.^bIn chloroform.^cIn deuteromethylene chloride.

The effect of intramolecular coordination has again been noted [24, 25]. A recent study [30] involved a series of phenyltin diethyldithiocarbamates where the coordination number of the tin varies between four and seven (in both solution and the solid state). ^{13}C chemical shift data are also presented, but unfortunately no J -values.

13.7 Compounds with Sn–B and Sn–N bonds (Table 13.5)

Values for only four compounds of this type appear to have been reported so far. Sn–B [31] and Sn–N [20] coupling constants have been measured in the solid state.

13.8 Coordination complexes derived from R_2SnCl_2 (Table 13.6)

Three studies have so far been published. One [32] involves nitrogen donors (pyridine, bipyridine, 1,10-phenanthroline) and shows the high field resonances expected for hexacoordination. A second [33] deals with nitroso-aromatic amines which coordinate via oxygen. Unfortunately no liquid state

Table 13.5 Compounds with Sn–B and Sn–N bonds

Compound	δ_{iso}	δ_{liquid}	Ref.
$(\text{Me}_3\text{Sn})_2\text{BN}(\text{Hex}^+)_2$	-144 ± 0.5 $J(\text{Sn–B}) 700 \pm 50$	-146.5	31
$\text{Me}_3\text{SnNSNP–Bu}_2^+$	46.2 $J(\text{Sn–N}) 105 \pm 5$		20
$\text{Me}_3\text{SnN}(\text{SO}_2\text{Me})_2$	73.6		20
$\text{Me}_3\text{SnN}(\text{SO}_2\text{Me})_2 \cdot \text{Me}_3\text{SnOH}$	94.8, 68.6		20, 54

Table 13.6 Coordination complexes of R_2SnCl_2

Compound	δ_{iso}	δ_{liquid}	Ref.
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{py}$	–309		24
$\text{Me}_2\text{SnCl}_2 \cdot \text{bipy}$	–267		24
$\text{Me}_2\text{SnCl}_2 \cdot \text{phen}$	–272	-109.5^a	24
$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{py}$	–389	-387.1^a	24
$\text{Ph}_2\text{SnCl}_2 \cdot \text{bipy}$	–383	-378.4^a	24
$\text{Ph}_2\text{SnCl}_2 \cdot \text{phen}$	–386		24
$\text{Me}_2\text{SnCl}_2 \cdot \text{ON–C}_6\text{H}_4\text{–NMe}_2$	–281.0		25
$\text{Me}_2\text{SnCl}_2 \cdot \text{ON–C}_6\text{H}_4\text{–NEt}_2$	–106.0		25
$\text{Me}_2\text{SnCl}_2 \cdot \text{ON–C}_6\text{H}_4\text{–NH}_2$	–254.8		25
$\text{Me}_2\text{SnCl}_2 \cdot \text{ON–C}_6\text{H}_4\text{–NMe}_2$	–277.6		25
$\text{Me}_2\text{SnCl}_2 \cdot \text{ON–C}_6\text{H}_4\text{–N} \begin{array}{c} \diagup \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_4\text{–NO}$	–95.2		25
$[\text{Ph}_2\text{SnCl}_3] [\text{Me}_4\text{N}]^+$	–236	–251	26

py = pyridine; bipy = bipyridine; phen = 1,10-phenanthroline.

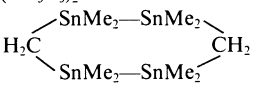
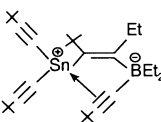
^aConcentrated solution.

data are given for comparison, but it was easy to distinguish between penta-coordinate tin (at about -100 ppm) and hexacoordinate tin (-250 to -280 ppm). A value for a triphenyldichlorostannate ion has also been reported [34].

13.9 Miscellaneous organotin compounds (Table 13.7)

Chemical shifts for a number of stannocenes have been obtained [35–37]. The

Table 13.7 Miscellaneous organotin compounds

Compound	δ_{iso}	δ_{liquid}	Ref.
Cp_2Sn	$-2162.8, -2224.4$	-2199.0	35
$(\text{Me}_5\text{C}_5)_2\text{Sn}$	$-2136.6, -2140.2$	-2129	36
	$-74.4, -77.5$ [$^1J(\text{Sn-Sn})$ 4245]	-78.5	6
$(\text{Ph}_5\text{C}_5)_2\text{Sn}$	-2215		37
$(\text{Ph}_4\text{HC}_5)_2\text{Sn}$	-2200		37
$(\text{Bz}_5\text{C}_5)_2\text{Sn}$	-2288	-2188	37
$[(4\text{-Bu'Ph})\text{Ph}_4\text{C}_5]_2\text{Sn}$	-2235		37
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CHSiMe}_3]_2$	room temp. 692 (77 K: 613)	165 K: 740/725	38
	-145.6	-154.2^a	39
$\text{ClSn}[(\text{CH}_2)_8]_3\text{SnCl}(\text{PhCH}_2)\text{Ph}_3\text{P}^+\text{Cl}^-$	128, -24	8	40
$\text{ClSn}[(\text{CH}_2)_6]_3\text{SnCl}\cdot\text{Bu}_4\text{N}^+\text{F}^-$	-50	-6.5	40
$[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]_\infty$	$-88, -118$		41, 42
$[(\text{Et}_3\text{Sn})_3\text{Co}(\text{CN})_6]_\infty$	-75		41
$[(\text{Et}_3\text{Sn})\text{Au}(\text{CN})_2]_\infty$	-64		41
$[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6]_\infty$	$-108, 46$		41, 43
$[(\text{Me}_3\text{Sn})_4\text{Ru}(\text{CN})_6]_\infty$	$-97, 32$		41, 43
$[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6\cdot 2\text{H}_2\text{O-dioxane}]_\infty$	$-136, -73$		41
$[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6\cdot n\text{H}_2\text{O}]_\infty$	47		41
$[(\text{Me}_3\text{Sn})_4\text{Os}(\text{CN})_6]_\infty$	$-94, 26$		43
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{Cl}$	146		44
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{Br}$	128.3		44
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{I}$	81.9		44
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{OSnR}'_3$	83		44
$(\text{P})-(\text{CH}_2)_6\text{SnBu}_2\text{OSnR}'_3$	81.6		44
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{R}'$	$-11.4, -12.0$		44
$(\text{P})-(\text{CH}_2)_6\text{SnBu}_2\text{R}'$	-12.2		44
$(\text{P})-(\text{CH}_2)_4\text{SnBu}_2\text{SnBu}_3$	$-83.0, -82.4$		44

^aIn deuteriomethylene chloride.

^bIn CFCl_3 .

^cIn chloroform.

(P) denotes polymer backbone, R' is not defined.

isotropic shifts in the solid (two non-equivalent sites in two cases [35, 36]) and in solution are almost identical. The same is true for 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane [6].

A detailed paper [38] has concerned itself with the nature of the tin–tin double bond in $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$, which is concluded to be based on a very weak dative interaction. In solution there is a monomer–dimer equilibrium; at 165 K two signals are present (no tin–tin coupling can be seen) and above 225 K no signal is visible. In the solid state $^1J(\text{Sn}–\text{Sn})$ is 1340 ± 10 Hz. The chemical shift is strongly temperature dependent.

Wrackmeyer *et al.* [39] have studied a zwitterionic compound (formally of the type R_3Sn^+) which also retains its structure in solution. Newcomb *et al.* [40] have looked at the complexation of halide ions by macrocyclic compounds $\text{ClSn}[(\text{CH}_2)_n]_3\text{SnCl}$ ($n=6, 8$). For $n=8$ complexation was carried out with $\text{PhCH}_2\text{PPh}_3^+ \text{Cl}^-$, and the chloride ion was isolated on one tin site as shown by the presence of signals at 128 and -24 ppm; in the case where $n=6$, $\text{Bu}_4\text{N}^+ \text{F}^-$ was used and it was clear that the fluoride ion is shared between the two tin sites (only one signal with tin–fluorine coupling).

Three papers [41–43] have concerned themselves with supramolecular tin compounds of the type $[(\text{Me}_3\text{Sn})_n\text{M}(\text{CN})_m]_\infty$ ($\text{M}=\text{Co}, \text{Au}, \text{Fe}, \text{Ru}, \text{Os}$) which often contain two different tin sites (trigonal bipyramidal and pseudo-tetrahedral).

There has been considerable interest in polymer-supported tin reagents in recent years, and it is surprising that solid state tin NMR has not until very recently [44] been used to characterize such species. The tin chemical shifts observed lie in the usual ranges, but the linewidths are very large, perhaps because the tin nuclei are attached at sites with differing geometries.

Some data for ‘bioorganotins’ have appeared [45].

13.10 Other measurements

Solid state NMR makes it possible to observe immobile products of reactions occurring at surfaces. A series of papers by Lefebvre and coworkers [46–50] has dealt with such surface chemistry. Thus Bu_3SnH has been shown [46] to react with a silica/alumina surface to form only $\equiv\text{Si}–\text{O}–\text{SnBu}_3$ linkages (δSn *c.* $+100$ ppm). The species observed when an alumina surface is used absorb at -171 and -227 ppm.

Another very recent paper [51] has involved rhenium-based metathesis catalysts (Re_2O_7 on silica/alumina) which were treated with tetraalkyltins (Me_4Sn , Et_4Sn , Bu_4Sn). Products were identified by solid state NMR (^{13}C , ^{119}Sn) and Mössbauer spectroscopy, and by analogy with results obtained by Lefebvre it was concluded that the species formed were of the type $\equiv\text{Si}–\text{O}–\text{SnR}_3$ ($\text{Me}=137$, $\text{Et}=100$, $\text{Bu}=103$ ppm).

13.11 ^{13}C measurements (Table 13.8)

Mention has already been made of the seminal paper by Lockhart *et al.* [7] in which $^1J(\text{Sn}-\text{C})$ was found to be a linear function of the angle $\text{C}-\text{Sn}-\text{C}$. In 1987, using an extended database, the equation was refined [52] to give

$$|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 10.7(\theta) - 778 \quad (r=0.975, n=28) \quad (13.2)$$

Remarkably, since then general use does not appear to have been made of this phenomenon. While ^{13}C chemical shift data have often been reported,

Table 13.8 One-bond tin–carbon coupling constants

Compound	$^1J(\text{Sn}-\text{C})_{\text{solid}}$	$^1J(\text{Sn}-\text{C})_{\text{liq}}$	Ref.	Compound	$^1J(\text{Sn}-\text{C})_{\text{solid}}$	$^1J(\text{Sn}-\text{C})_{\text{liq}}$	Ref.
<i>Tetraordinate</i>				<i>(o-\text{CF}_3\text{C}_6\text{H}_4)_2\text{SnCl}</i>	679	652	57
Ph_4Sn	531		57	<i>(p-\text{CF}_3\text{C}_6\text{H}_4)_2\text{SnCl}</i>	623	596	57
<i>(m-\text{CF}_3\text{C}_6\text{H}_4)_2\text{Sn}</i>	544	520	57	$\text{MeO}_2\text{C}(\text{CH}_2)_2\text{SnCl}_3$	720		18
<i>(p-\text{CF}_3\text{C}_6\text{H}_4)_2\text{Sn}</i>	535	511	57	$\text{MeO}_2\text{C}(\text{CH}_2)_3\text{SnCl}_3$	768		18
$[(3,5\text{-CF}_3)_2\text{C}_6\text{H}_3]_2\text{Sn}$	546	521	57	$\text{MeO}_2\text{C}(\text{CH}_2)_3\text{SnCl}_3$	784		18
$(\text{Hex}')_4\text{Sn}$	301.6	306.3	10	Ph_2SnCl_2	785		57
Ph_3SnMe	510 (to phenyl carbons)		52	<i>Hexacoordinate</i>			
$\text{Ph}_2\text{SnMe}_2 \cdot 2\text{Cr}(\text{CO})_3$	380		52	$\text{Me}_2\text{Sn}(\text{S}_2\text{PMe}_2)_2$	470		52
Ph_6Sn_2	413	395	57	$\text{Me}_2\text{Sn}(\text{S}_2\text{COEt})_2$	570		52
$(\text{Me}_2\text{SnS})_3$	430		7, 52	$\text{Me}_2\text{Sn}(\text{ON}(\text{H})\text{COCH}_3)_2$	600		52
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnMe}_3^c$	360 (SnMe_3), 397 ($\text{Sn}-\text{C}\equiv$)		53	$\text{Me}_2\text{Sn}(\text{oxinate})_2$	630		7
<i>Pentacoordinate</i>				$\text{Me}_2\text{Sn}(\text{OAc})_2$	660		52
$\text{Me}_3\text{Sn}[\text{ON}(\text{Ph})\text{COPh}]$	410		52	$\text{Me}_2\text{Sn}(\text{NCS})_2$	670		52
$\text{Me}_2\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{O}$	430, 315		52	$\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$	670		52
$\text{Me}_2\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{NMe}$	465, 325		52	$\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	680		52
Me_2SnCl	470		7, 52	$[\text{Me}_2\text{SnCl}_2\text{-salicyl-aldehyde}]_2$	680		52
$\text{Me}_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$	490		52	$\text{Me}_2\text{Sn}[(\text{S}_2\text{CN}(\text{CH}_2)_4)_2]$	705 ± 10		52, 55
$\text{Me}_3\text{Sn}[\text{O}_2\text{C}(1\text{-naphthyl})]$	490		52	$\text{Me}_2\text{Sn}(\text{laurate})_2$	720		52
Me_3SnNO_3	500		52	$\text{Me}_2\text{SnPO}_4\text{H}$	780		52
$\text{Me}_3\text{Sn}[\text{O}_2\text{C}(\text{Hex}')]]$	510 (av.)		52	$\text{Me}_2\text{SnCl}_3(\text{lutidine-N-oxide})_2$	810		7
$\text{Me}_3\text{Sn}[\text{O}_2\text{C}(p\text{-C}_6\text{H}_4\text{NH}_2)]$	530		52	$\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	675	668 ^a , 675 ^b	56
Me_3SnOAc	540		7, 52	$\text{Me}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{Cl})_2\text{O}$	820		52
Me_3SnF	550		52	$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMF}$	990		7
$[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]_\infty$	570, 550		33	$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMSO}$	1060		7
$[(\text{Me}_3\text{Sn})_2\text{CO}_3]_n$	590		52	$\text{Me}_2\text{SnCl}_2 \cdot 2\text{pyridine-N-oxide}$	1120		52
Me_3SnOH	600		52	$\text{Me}_2\text{Sn}(\text{acac})_2$	1175	966 ^a , 929 ^b	7, 56
$\text{Me}_2\text{PhSnOAc}$	610		7	$\text{MeSn}(\text{Cl})(\text{S}_2\text{CNMe}_2)_2$	950 ± 50		52
$\text{Me}_2\text{Sn}(\text{Cl})(\text{S}_2\text{CNMe}_2)$	580		52	$[\text{MeSn}(\text{O})\text{OH}]_n$	1160, 1030		52
$\text{Me}_2\text{Sn}(\text{Cl})(\text{cysteine ethyl ether})$	600		52	$[\text{Me}_2\text{Sn}(\text{OAc})_3][\text{NMe}_4]^+$	c. 866, 820		16
$\text{Me}_2\text{Sn}(\text{glycyl-methioninate})$	640		52	<i>Heptacoordinate</i>			
$\text{Me}_2\text{Sn}(\text{NO}_3)(\text{OH})$	730		52	$\text{MeSn}(\text{S}_2\text{CNEt}_2)_3$	1015		53
$(\text{Me}_2\text{SnO})_n$	660		52				52
Ph_3SnCl	613	587	57				

^aIn chloroform.

^bIn benzene.

^cAt 297 K.

coupling constants have not. Since the chemical shift data do not generally provide useful structural information when shifted by a small amount on going from solution to the solid state, they have not been tabulated here. Only values of $^1J(\text{Sn}-\text{C})$ are listed in Table 13.8, as they provide the most diagnostic structural information and can most easily be determined accurately. The compounds are ordered according to their coordination number as in Ref. 52.

Sebald and coworkers [53, 54] have carried out detailed studies involving motions of the Me_3Sn propellers in the solid state.

13.12 Inorganic tin compounds

Measurements on inorganic tin compounds are possible, though measurement times may become very long because cross-polarization is not available. A systematic treatment of the results such as has been attempted above is not possible, so that only a brief summary of the type of studies carried out will be given, this time arranged in chronological order. References to other work can be found in the cited papers.

A series of ternary tin oxides has been examined [59], and a later paper [60] demonstrates that neodymium tin oxide, samarium tin oxide and a mixed yttrium samarium tin oxide function as sensitive chemical shift thermometers. Amorphous and microcrystalline layered metal(IV) hydrogenphosphates have been studied [61]. Single compounds have been looked at in detail, such as tin(II) bisfluorosulphate [62] and tin hexathiohypodiphosphate [63]. Tin(II) polypyrazolylborate complexes have been looked at in both the solid state and solution [64]. Another recent study has involved $\text{Al}_2\text{O}_3/\text{SnO}_2$ systems [65].

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14 ^{119}mSn Mössbauer studies on tin compounds

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14.1 Introduction

Information extracted from ^{119}Sn Mössbauer spectroscopy of tin compounds essentially concerns (1) the valence state in inorganic derivatives, (2) structure and bonding in the metal environment (mainly in organotins) and (3) the dynamics of tin nuclei, the latter possibly correlated to the nature of the substrate (mono- or polymeric). Measurements are effected on solids (crystalline as well as amorphous), gels and solutions (frozen to glassy phases). It then appears that Mössbauer spectroscopic measurements give information analogous, or complementary, to data gained from other spectroscopic techniques, such as NMR spectroscopy, X-ray diffractometry, neutron diffraction, etc. There are advantages, as well as disadvantages, in the data extracted from Mössbauer spectroscopy: the first concerns, *inter alia*, the easy experimental procedures, the simple and inexpensive instrumentation, the possibility of obtaining information about the metal properties in high molecular weight systems; the second lies essentially in the time needed to collect a spectrum (~ 1 day). In fact, the circumstance that the absorber samples must contain Sn at the milligram level [about $0.5(\text{mg } ^{119}\text{Sn})\text{cm}^{-2}$], and the near impossibility of quantitative Sn analysis, are common to other widely employed spectroscopic techniques.

As stated in the preface, this book is addressed to academic researchers, analytical chemists and scientists in industry. Thus the statements by many authors of treatises [1–14], as well as of chapters in collections [15–20], hold even in the present context: according, for example, to the introduction by Ruby (in Ref. 9, p. 1), besides ‘. . . the skilled, knowledgeable Mössbauer researcher’, who does not need any introduction or theoretical treatment, ‘another class of readers of this book will be people with little, if any, Mössbauer experience and knowledge. Perhaps the graduate student . . .’ Accordingly, we report here only a very brief survey of the theoretical background, referring to detailed treatments reported in the literature for those who want to be better acquainted with the matter [1–15].

As far as our students were concerned, in lectures we introduced the Mössbauer effect by the wonderful ‘cartoons’ by Debrunner and Frauenfelder (in Ref. 4, p. 1), followed by a descriptive treatment of experi-

mental results and related implications [21]. According to our experience, this was sufficient in order to understand the basic concepts and to allow treatment of the original papers on the various fingerprint applications. Besides, the main part of our courses was devoted to showing how to deal with physical models and the related mathematical language; for example, the definition of the recoil free fraction f ,

$$f = \exp(-k^2 \langle x^2 \rangle) \quad (14.1)$$

where k = wave vector of γ -rays and $\langle x^2 \rangle$ = mean square displacement of the Mössbauer nucleus, was reached through the treatment by Frauenfelder [1] and Wertheim [2], each step being fully explained and understood by recalling any necessary mathematics and physics from textbooks and booklets; as a consequence, our students in chemistry became aware that their general scientific knowledge was sufficient to comprehend the theoretical aspects of the principles of Mössbauer spectroscopy. We believe the latter holds for any concerned chemist.

Further information reported here deals with the instrumentation, experimental procedures, the various spectral shapes and the related computer fit. Then, taking recent measurements into account, fingerprint criteria for the assignments of valence state, as well as of coordination number and structure, are presented. Rationalization of isomer shift (δ) parameters via δ -ligand electronegativity correlations is reported, and the point-charge model treatment of the parameter nuclear quadrupole splitting, ΔE , for configurational assignments in the neighborhood of tin is treated in relation to recent reports. Then, the 'monomer-polymer' fingerprint through the temperature dependence of the area under the resonant peaks is presented, in the context of studies on the dynamics of tin nuclei. Lastly, applications to materials research and environmental studies, to interactions of organotin(IV) with biological molecules and systems, and to organotin(IV) derivatives in frozen solutions, are sketched.

In conclusion, all information reported in the present chapter is intended to (1) guide the interested reader to the existing collection and treatment of ^{119}Sn Mössbauer data [5, 6, 8, 17–20, 22–27] and (2) give information on the procedures concerning the determination and rationalization of the ^{119}Sn Mössbauer parameters, hopefully also to be carried out by non-Mössbauer specialists. The examples of data collection reported here (section 14.10), as well as data discussed in the text (e.g. sections 14.5 and 14.6), essentially concern the years after 1983–86 (i.e. the apparent deadlines in the last published reviews [19, 20]), as well as data not previously reported. A complete and detailed listing is reported in the *Mössbauer Effect References and Data Journal* by Stevens [28]. Reference is also made to the collection of data on organotin compounds, including Mössbauer spectroscopic data, in the *Gmelin Handbook on Inorganic and Organometallic Chemistry* [29].

14.2 Hyperfine interactions and parameters

The effect discovered by Rudolf Mössbauer in 1957 consists of the ‘nuclear resonance fluorescence of gamma radiation’, analogous to atomic fluorescence of UV–vis light [30]; the effect is now generally termed as the recoil-free emission and resonant absorption of nuclear gamma rays [2]. Absorption spectra are measured by the apparatus and techniques described in section 14.3 [16, 31–34; see also 1, 2, 5–8, 10, 11]; the energy scanning occurs via the Doppler effect due to motion of the source.

By employing a $\text{Ca}^{119}\text{SnO}_3$ source (section 14.3) and a CaSnO_3 absorber, a spectrum such as (a) in Figure 14.1 is obtained; with a different absorber, e.g. $(\text{CH}_3)_4\text{Sn}$, spectrum (b) occurs. The difference in energy between the dips of the $(\text{CH}_3)_4\text{Sn}$ and CaSnO_3 lines, (b) and (a) in Figure 14.1, (the latter being taken as the zero energy point), is defined as the ‘isomer shift’ or ‘center shift’, δ . A different absorption spectrum is obtained employing as absorber $(\text{CH}_3)_3\text{SnCl}$, which is shown in Figure 14.2. Two absorption lines are observed to occur; the energy difference between the two dips is the ‘nuclear quadrupole splitting’ parameter, ΔE . Absorption spectra such as those in Figures 14.1 and 14.2, i.e. one- or two-line spectra, are generally detected for tin compounds and complexes; δ and ΔE are the related hyperfine parameters.

The hyperfine interaction effecting isomer shifts in one-line spectra, such as in Figure 14.1, is sketched in Figure 14.3. It consists of the ‘interaction energy between the total electronic charge and the electrostatic potential generated by the nucleons’ [35] being ‘manifestation of a very specific feature of the

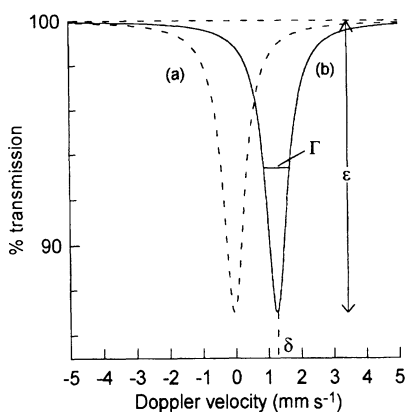


Figure 14.1 Simulated ^{119}Sn Mössbauer spectra of (a) CaSnO_3 and (b) $(\text{CH}_3)_4\text{Sn}$. δ = isomer shift with respect to RT. CaSnO_3 , mm s^{-1} ; ϵ = % resonant effect; Γ = full width at half height of the resonant peaks. Lorentzian line shapes. Area under the resonant peaks = $(\pi/2)\epsilon\Gamma \text{ mm s}^{-1}$. For $(\text{CH}_3)_4\text{Sn}$, $\delta = 1.31 \text{ mm s}^{-1}$, average value from Ref. 25. $1 \text{ mm s}^{-1} = 7.9625 \times 10^{-8} \text{ eV}$.

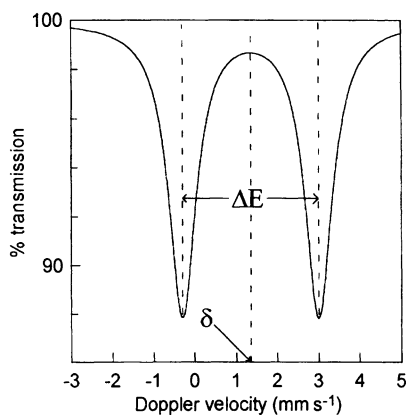


Figure 14.2 Simulated spectrum of $(\text{CH}_3)_3\text{SnCl}$. The isomer shift $\delta = 1.39 \text{ mm s}^{-1}$ is the energy difference between the spectrum centroid and the CaSnO_3 zero point; the nuclear quadrupole splitting $\Delta E = 3.30 \text{ mm s}^{-1}$ is the energy difference between the two component lines. δ , ΔE : average values from Ref. 25.

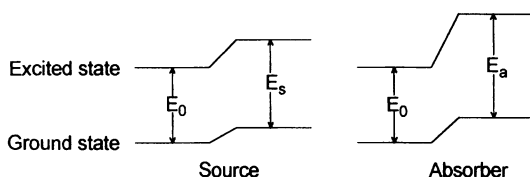


Figure 14.3 Isomer shift: $\delta = E_a - E_s$. The electric monopole interaction shifts the nuclear levels. (Adapted from Ref. 2; see also Refs 6, 9–11, 17, 35–41.)

hyperfine interaction between nuclear and electronic charges; namely, the effect of the finite nuclear size on the Coulomb energy' [35].

The isomer shift δ is defined as [2, 5, 6, 8, 10, 11, 16–18, 20, 35–40, 42].

$$\delta = K(\delta R/R) \{ [\psi(0)_s]_a^2 - [\psi(0)_s]_s^2 \} \quad (14.2)$$

where $[\psi(0)_s]^2$ are the total s -electron densities at the absorber (a) and source (s) atoms; K is a constant term characteristic for any given isotope (the ^{119}Sn value would be employed here); δR is equal to $R_{\text{ex}} - R_{\text{ground}}$ (the radii of excited and ground nuclear states, respectively). Then δ depends upon a nuclear factor, $\delta R/R$, and an extranuclear factor, the s -electron density. For ^{119}Sn , δR is positive; then for $[\psi(0)_s]_a^2 > [\psi(0)_s]_s^2$, δ assumes positive values.

The hyperfine interaction between a nucleus with a quadrupole moment eQ and the external electric field gradient splits the degeneracy of the nuclear $3/2$ level (Figure 14.4), effecting the energy transition ΔE , the nuclear quadrupole splitting; the latter appears to yield two-line spectra in, for example, tin derivatives, as in Figure 14.2. ΔE values are then experimentally determined,

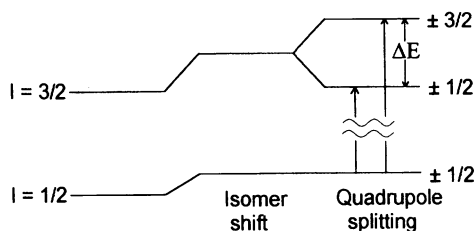


Figure 14.4 Nuclear quadrupole splitting, ΔE . The electric field gradient (EFG) tensor splits the nuclear spin degeneracy. (Adapted from Ref. 2; see also Refs 5, 6, 8, 10, 11, 16–18, 36–39, 41, 43.)

being defined by the eqn 14.3 [2, 5, 6, 8, 10, 11, 16–18, 20, 36–39, 42–44]:

$$|\Delta E| = \frac{1}{2} e^2 q Q (1 + \eta^2/3)^{1/2} \quad (14.3)$$

where eQ is the quadrupole moment of the nucleus; $eq = V_{zz}$ is (–) the z -component of the electric field gradient, EFG, at the nucleus; $e = 4.8 \times 10^{-10}$ e.s.u. is the protonic charge; $\eta = (|V_{xx} - V_{yy}|)/V_{zz}$ is the asymmetry parameter, $V_{\alpha\alpha}$ being the diagonal elements of the EFG tensor. For ^{119}Sn nuclei, the sign of ΔE is opposite to that of V_{zz} , due to the negative sign of Q .

14.3 Instrumentation and experimental procedures

14.3.1 Instrumentation

Detailed information on instrumentation for Mössbauer experiments has been reported since 1964 by Wertheim [45] and by other workers [31–34, 46–54].

Sophisticated and reliable apparatus are nowadays employed (Figure 14.5).

14.3.2 Experimental procedures

In carrying out a Mössbauer experiment, attention must be devoted to certain experimental procedures, the most important of which are (1) the thickness of the absorbers, (2) the determination of the zero point and (3) the calibration of the velocity.

Thickness of the absorbers. For a complete overview of thin absorber theory, the reader is referred to the elegant and complete treatment developed by Goldanskii and Makarov [36]. It must be recalled that the entity of the observed Mössbauer effect is influenced by the effective thickness of the absorber, so that for a satisfactory ^{119}Sn Mössbauer experiment, the concentration must not exceed $\sim 0.5 (\text{mg } ^{119}\text{Sn}) \text{ cm}^{-2}$. This ^{119}Sn concentration takes

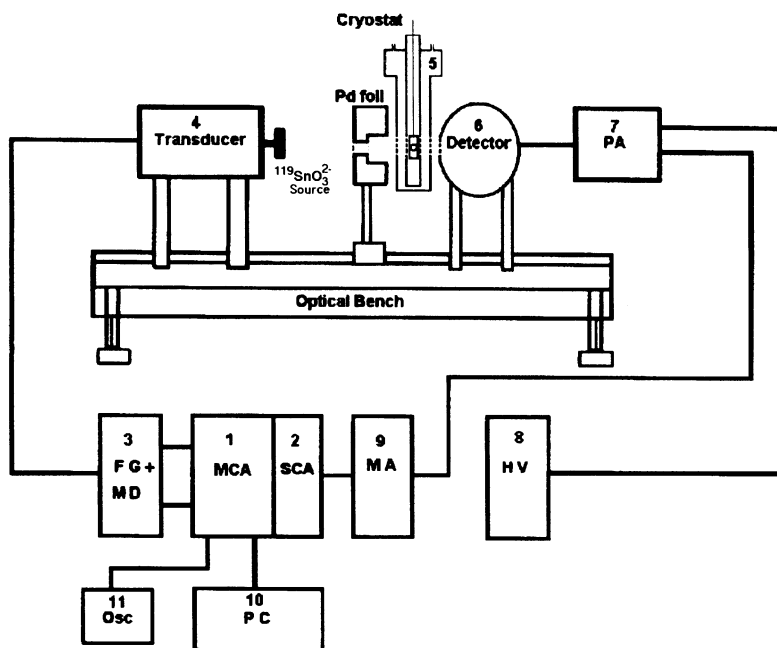


Figure 14.5 Schematic diagram of a ^{119}mSn Mössbauer apparatus. 1: Multichannel analyzer (MCA); 2: single channel analyzer (SCA); 3: function generator and timing control, motor driver with dynamic control (FG, MD); 4: electromagnetic linear transducer with ^{119}Sn source; 5: (liquid nitrogen or helium) cryostat, with absorber holder and temperature controller; 6: detector (proportional counter, NaI(Tl), etc.); 7: charge preamplifier whose characteristics are adapted to the detector (PA); 8: high voltage generator, shaping amplifier, windows discriminator, spectrum stabilizer (HV); 9: main amplifier; 10: personal computer with RS/c interface (PC); 11: oscilloscope as monitor of multichannel (Osc). (Adapted from Ref. 53.)

into account the influence of the absorber thickness on the fractional absorption, on the broadening of the absorption bands and finally on the photoeffect-induced attenuation [51]. As far as absorbers with low concentrations of Mössbauer nuclei are concerned, i.e. in frozen solutions, a treatment of the optimal thickness of the absorber and of the minimum measurement time has been reported by Vértés *et al.* [52].

Determination of the zero velocity channel. Determination of the zero velocity channel, together with the velocity calibration, are crucial for calculating reliable Mössbauer parameters. The simplest way to determine the zero velocity channel is to perform a single-line spectrum measurement by using a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source, commercially available, and MSnO_3 ($\text{M} = \text{Ca}$ or Ba) standard absorbers, in some cases ^{119}Sn enriched. The subsequent folding of the two halves of the resulting Mössbauer spectrum, by using an appropriate computational method, allows the calculation of the 'zero point' of the multi-

channel analyzer. As an alternative to MSnO_3 absorbers, some researchers use a tin foil; in such cases, care has to be taken when calculated δ -values are compared.

Velocity calibration. Calibration of the velocity, i.e. determination of the velocity for each data point, may be performed very cheaply by measuring the magnetic hyperfine splitting of the ^{57}Fe resonance in natural or enriched metallic iron. In fact, a Mössbauer spectrum of iron foil, carried out at room temperature by using a ^{57}Co source, in a Pd matrix, shows a magnetic six-line pattern, from which the velocity calibration may be obtained taking into account the magnetic hyperfine splittings between the third and the fifth line, the second and the fourth line ($g_{\text{lav}} = 3.9156 \pm 0.0017 \text{ mm s}^{-1}$ in both cases [55]), or between the first and the last lines (10.167 mm s^{-1} [51]).

14.3.3 Sources

As mentioned in the section on the determination of the zero velocity channel, $^{119\text{m}}\text{Sn}$ Mössbauer sources (half-life 245 days) (e.g. Ref. 55) are used; calcium stannate, $\text{Ca}^{119}\text{SnO}_3$, is the best matrix, having at room temperature a good recoilless fraction (*c.* 0.5), minimal internal electronic absorption and narrow linewidth (ranging from 0.4 to 0.5 mm s^{-1} , for activity varying from 1.5 up to 7.5 mCi cm^{-2}) [55]. Cobalt-57 sources of high specific activity, in various matrices, are commercially available, being employed for ^{57}Fe Mössbauer measurements.

14.4 Treatment of spectral data

Many articles and reviews have been published dealing with techniques for the reduction and refinement of Mössbauer spectra. An exhaustive review by Vandenberghe [56] was recently published.

A Mössbauer spectrum (section 14.2) is described by a transmission integral resulting from the convolution of a source Lorentzian function and an absorber function, which in turn is described by an exponential of the sum of absorber Lorentzian lines [57]. For a single line source, a 'powder' spectrum consisting of N_0 absorption lines may be described by eqn 14.4 [56, 58]:

$$N(x) = N(\infty) \left[1 - \frac{2f_s}{\pi\Gamma_s} \int_{-\infty}^{+\infty} \frac{dE}{1 + (2E/\Gamma_s)^2} \times \left(1 - \exp \left\{ \sum_{n=1}^{N_0} \frac{-\alpha_n T}{1 + 4[(E + \delta + \beta_n - x)/\Gamma_a]^2} \right\} \right) \right] \quad (14.4)$$

where $N(x)$ and $N(\infty)$ are the counts recorded at channel x of the multi-channel analyzer and the off-resonance counts (the baseline), respectively; f_s ,

is the source resonance fraction; T is the effective absorber thickness; Γ_s and Γ_a are the full widths at half height for the source and absorber lines, respectively; δ is the centroid of the spectrum; and α_n and β_n are the intensity and the position of the n th hyperfine component of the absorber quadrupole pattern.

When the effective thickness of the absorber (section 14.3) is small ($T \rightarrow 0$), the exponential term in eqn 14.4 may be approximated by the first two terms of its series expansion, reducing the transmission integral to a sum of Lorentzian lines.

In the majority of experiments the 'thin absorber approximation' is quite satisfactory, but deviations from the ideal Lorentzian shape may occasionally originate from instrumental factors, such as (1) the velocity noise caused by spurious vibrations, produced, for example, by cryogenerators [59], (2) the 'cosine smearing' of the velocity of the source over the angle $\vartheta = \arctan(R/L)$, where R and L are the radius of the collimator and its distance from the source [60] and (3) the use of an inadequate number of channels in collecting the spectra [56]. Saturation effects, especially in the case of ill-resolved spectra, may alter the Mössbauer parameters, even for absorbers commonly regarded as 'thin' [61]. Instrumental noise may be drastically reduced taking the proper precautions; if some deviations persist, however, analysis of the data must be performed after correction by, for example, deconvoluting the spectrum by means of the fast Fourier transform techniques in order to remove the distortion [56]. Alternatively, the uncorrected data may be fitted with appropriate line shapes obtained from distorted standard spectra [56].

A generic fitting program is based on an efficient minimization routine (using e.g. a Levenberg-Marquardt or Gauss-Newton algorithm), which alters the initial estimates of the free parameters in order to minimize the weighed mean-square deviation χ^2 between the experimental data points Y_i^{exp} and the corresponding theoretical values Y_i^{theo} . The use of appropriate constraints allows a reduction of the number of free parameters, leading to a more efficient use of the computer. For complex spectra it is often essential to impose a number of constraints in order to get the spectrum to converge.

It is worth remarking here that χ^2 is not a good criterion for comparison between different spectra because the value of χ^2 may depend on the precision to which the spectrum is determined, being usually 'improved' by using lower quality data. This difficulty arises [62] because χ^2 does not measure how well the assumed function matches the true function, and the theory is better tested by data of high quality, the difference between the true and assumed functions being more evident when the data are less spread by random deviations. Ruby [60] has suggested the use of the parameter 'misfit', which does not appear to improve the goodness of fit with poorer data, and facilitates comparison between a single theory and several measurements of varying quality. Many groups use 'home-made' programs adapted to treat specific

problems. Commercial programs are also available, such as Specfit, Mosfun, Moss90 and the versatile SITE and DIST programs of the Normos Package, which were developed to solve the common problems encountered in Mössbauer spectroscopy. Programs for Mössbauer–Zeeman spectrum fitting (combined magnetic dipole and electric quadrupole interactions, section 14.7.2) have been described [63, 58].

A general flow diagram of the fitting programs is shown in Figure 14.6.

14.5 Isomer shift: fingerprint criteria

The ^{119}Sn Mössbauer parameter isomer shift, δ , (eqn 14.2) essentially accounts for the oxidation state of tin. In fact, δ -values for Sn^{II} derivatives are larger than for Sn^{IV} , according to eqn 14.2, where high $[\psi(0)]_a$ is dictated by Sn^{II} $5s^2$ electrons. In $\text{R}_n\text{Sn}^{\text{IV}}$ compounds ($n=1-4$) $[\psi(0)]_a$ would depend upon C–Sn bond electrons. Within congeneric series, variations of δ -values are not, generally speaking, meaningful from a structural point of view concerning the environment of tin atom [5]. Values of δ for Sn^{II} , Sn^{IV} and $\text{R}_n\text{Sn}^{\text{IV}}$ derivatives, recently reported (1986–95), are shown in Table 14.1, and the related δ -ranges are represented in Figure 14.7, essentially corresponding to previous literature data quoted in earlier collections [20, 25], including $\text{R}_n\text{Sn}^{\text{II}}$ derivatives [20].

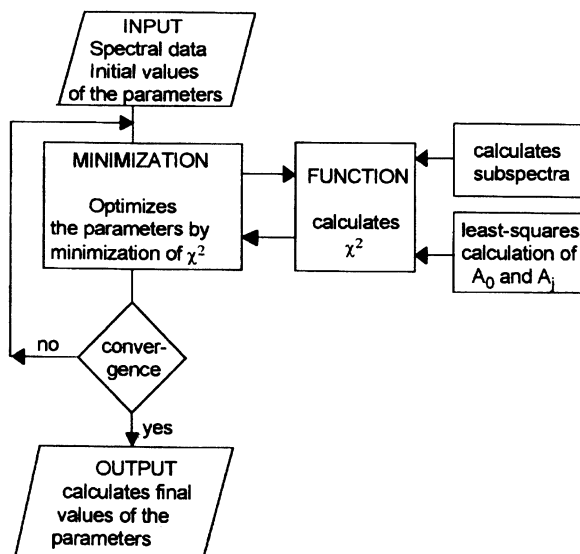


Figure 14.6 Flow diagram for fitting programs of Mössbauer spectra. A_0 , A_i : coefficients of the two terms of the exponential series of the transmission integral. (Adapted from Ref. 56.)

Table 14.1 Examples of limiting δ -values for tin(II), tin(IV) and organotin(IV) derivatives

Class	Compound ^a	δ^b (mm s ⁻¹)	Ref.
Sn ^{II}	(Me ₄ N) ₂ [Pd(SnCl ₃) ₅]	1.80	1
	Sn ^{II} [Sn ^{IV} (SO ₃ F) ₆]	4.48	2
Sn ^{IV}	CaSnF ₆	-0.48	3
	Sn(SCH ₂ CH ₂ S) ₂	1.40	4
R ⁺ Sn ^{IV}	(<i>o</i> -Cl-C ₆ H ₄) ₂ Sn(Ox) ₃	0.52	^c
	MeSnCl ₂ [(η^5 -C ₅ H ₅) ₂ Mo(H)]	1.80	5
R ₂ Sn ^{IV}	(<i>p</i> -Me-C ₆ H ₄) ₂ SnCl ₂ (dmpb)	0.75	6
	[Et ₂ Sn(Hmimt) ₄](NO ₃) ₂	1.81	7
R ₃ Sn ^{IV}	(<i>p</i> -tolyl) ₃ Sn[ON(Ph)COPh]	0.86	8
	Cy ₃ Sn[O ₂ C(C ₆ H ₄ - <i>p</i> -Me)]	1.72	9
R ₄ Sn ^{IV}	(Me ₃ SiC \equiv C) ₄ Sn	0.82	10
	MeSn[CH ₂ CH ₂ CH ₂) ₃ N]	1.40	11

^aR = organic radical; Me = methyl; Et = ethyl; Ph = phenyl; Cy = cyclohexyl; Ox = 8-oxyquinoline; dmpb = 4,4'-dimethyl-2,2'-bipyridyl; Hmimt = 1-methyl-2(3*H*)-imidazolinethione.

^bIsomer shift with respect to RT, CaSnO₃, BaSnO₃ or SnO₂, referred to solid state absorbers at liquid nitrogen temperature, unless otherwise stated in the cited references. Low and high δ -values in each class are reported, taken from literature data 1986–1995.

^cR. Schmiedgen *et al.*, personal communication.

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It clearly appears that the oxidation state, Sn^{II} or Sn^{IV}, is assigned with certainty through δ -values, while the data for R_{*n*}Sn^{IV} mutually correspond.

The occurrence of outlier δ -terms has been reported and commented on by Zuckerman [27]. Examples for recently reported data (not included in the δ -ranges of Table 14.1 and Figure 14.7) are as follows:

- $\delta = 1.358 \text{ mm s}^{-1}$ has been reported for tetrakis[*p*-(diethylamino)-phenyl]porphyrinato-SnFe(CO)₄. This low δ -value for a tin(II) derivative has been attributed to an important covalent character of the Sn–Fe bond [64].
- δ for Cp₂Ta(H₂)SnCl₃ (Cp = cyclopentadienyl) is 1.94 mm s^{-1} . Such tin(IV) δ -values have been attributed ‘unambiguously’ to the presence of covalent M–Sn bonds in this class of compounds [65].

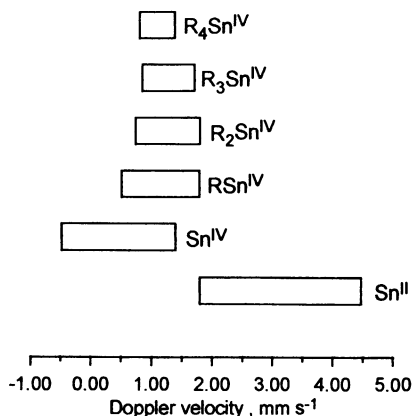


Figure 14.7 Approximate ranges of ^{119}Sn isomer shifts, δ , observed in tin compounds [relative to MSnO_3 ($\text{M}=\text{Ba}, \text{Ca}$) at room temperature]. Data ranges are estimated from the following number of δ -values reported in the literature (1986–1995): Sn^{II} : 64 (31 refs); Sn^{IV} : 238 (62 refs); RSn^{IV} : 63 (24 refs); $\text{R}_2\text{Sn}^{\text{IV}}$: 633 (124 refs); $\text{R}_3\text{Sn}^{\text{IV}}$: 591 (65 refs); R_4Sn : 81 (18 refs). (L. Pellerito *et al.*, in preparation.)

- $\delta = 0.27 \text{ mm s}^{-1}$ has been determined for $\text{PhSnCl}_3(\text{Ph}_2\text{PCpFeCpPPh}_2)$ [66].
- $\delta = 0.70 \text{ mm s}^{-1}$ for $(\text{Bu}_4\text{N})_2[(\text{Ph}_2\text{Sn})_2(\text{OH})_2(\text{MoO}_4)_2]$ [67]; $\delta = 2.01 \text{ mm s}^{-1}$ for the organotin(IV) moiety in $(\text{CH}_3)_2\text{Sn}[\text{Sn}(\text{SO}_3\text{F})_6]$ [68].
- $\delta = 0.58 \text{ mm s}^{-1}$ for $\text{Ph}_3\text{Sn}(\text{O}_2\text{CCH}_2\text{S}_2\text{CNEt}_2)$ has been calculated in ‘a three line spectrum fitted as two doublets sharing a common lower-velocity wing’ [69].

14.6 Nuclear quadrupole splitting: fingerprint criteria

The magnitude of ^{119}Sn Mössbauer nuclear quadrupole splitting parameters ΔE (eqn 14.3) depends mainly upon the component of the electric field gradient tensor along the z -axis, V_{zz} , which is influenced by the stereochemistry of the investigated compound and the nature of bonding between tin and ligand atoms (σ - or π -bonding may provoke different occupancy of both $5p$ and $5d$ orbitals) [5].

As for the isomer shift ranges (section 14.5) the choice of the limiting ΔE values in Figure 14.8 and Table 14.2 for tin and organotin derivatives, in given structural configurations, is based on data reported in the last 10 years (1986–95). Structural geometries are advanced from spectroscopic studies, including Mössbauer ΔE values, and/or determination by X-ray investigations.

The ΔE data in Table 14.2 and Figure 14.8 correspond essentially to previous literature reports [20, 25] as well as to earlier tabulations [17, 18, 70–72], except for a series of $\Delta E = 0.00$ values reported by Smith [25] for

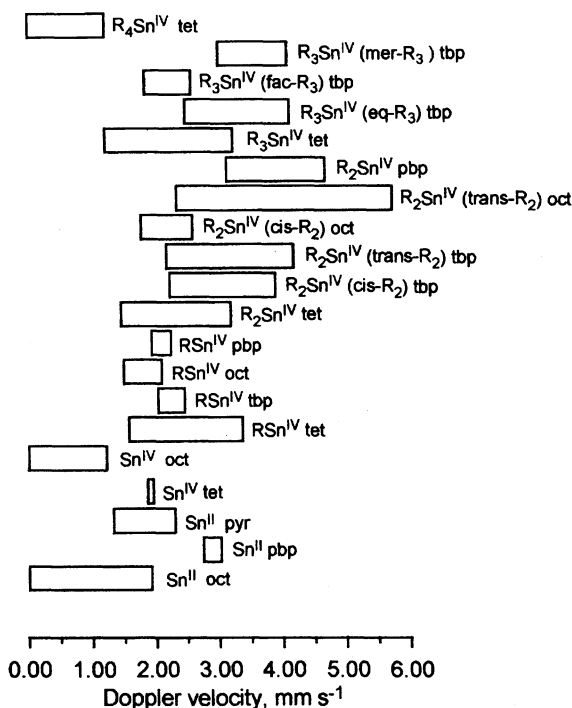


Figure 14.8 Approximate ranges of ^{119}Sn nuclear quadrupole splittings, ΔE , observed in tin compounds as a function of assumed structures. Data ranges are estimated from the following number of ΔE values reported in the literature (1986–1995): Sn^{II} : 64 (31 refs); Sn^{IV} : 238 (62 refs); RSn^{IV} : 63 (24 refs); $\text{R}_2\text{Sn}^{\text{IV}}$: 633 (124 refs); $\text{R}_3\text{Sn}^{\text{IV}}$: 591 (65 refs); R_4Sn : 81 (18 refs); tet=tetrahedral; pyr=pyramidal; tbp=trigonal bipyramidal; oct=octahedral; pbp=pentagonal bipyramidal; eq=equatorial; fac=facial. (L. Pellerito *et al.*, in preparation.)

$\text{R}_n\text{Sn}^{\text{IV}}$ ($n=1-3$). Large ΔE values, $\geq 5.00 \text{ mm s}^{-1}$, are not uncommon for organotin(IV) derivatives, as commented upon by Zuckerman [27].

14.7 Structure and bonding

Information concerning the environment of Mössbauer nuclei may be obtained through the rationalization of the hyperfine parameters δ and ΔE , defined in section 14.2, as outlined in the following.

14.7.1 Isomer shift

The isomer shift, δ (eqn 14.2) is dictated by the $5s$ electron density at Sn absorber nuclei, $[\psi(0)]_a$, in tin derivatives. The rationalization of ^{119}Sn δ -parameters in terms of the bonding situation at Sn, as well as in terms of

Table 14.2 Examples of ΔE values for tin(II), tin(IV) and organotin(IV) derivatives

Class	Geometry ^a	Compound ^b	ΔE^c (mm s ⁻¹)	Ref.
Sn ^{II}	tbp ^d	Sn ^{II} ₄ [Sn ^{IV} O ₂ (O ₂ CCF ₃) ₈]	1.78	1
	oct ^e	Cs ₄ SnBr ₆ , CsSnBr ₃	0.00	2
		Sn ^{II} ₂ Sn ^{IV} ₂ (H ₂ Thor) ₁₂	1.91	3
		(C ₁₀ H ₈ N ₂)Sn[(Me ₃ Si) ₂ C ₂ B ₄ H ₄]	2.73	4
	pyr ^g	(C ₁₀ H ₈ N ₂)Sn[(Me ₃ Si)(Me)C ₂ B ₄ H ₄]	3.01	4
		Sn(saldph)	1.32	5
Sn ^{IV}	tet	Sn(O ₂ CCF ₃) ₂	2.29	1
		SnCl ₃ [(η^1 -C ₅ H ₅) ₂ Mo(H)]	1.85	6
		SnCl ₃ [(η^1 -C ₅ H ₅) ₂ Ta(H ₂)]	1.94	7
	oct	Sn(SPyN) ₄	0.00	8 ^h
		PcSnI ₂	1.21	9
		[SnCl ₂ (Hdaptsc)]Cl	0.66	10
R ⁺ Sn ^{IV}	tet	[(Me ₃ Si) ₃ C]SnBr ₃	1.56	11
		MeSnCl ₂ [(η^5 -C ₅ H ₅) ₂ Mo(H)]	3.35	6
		Bu ⁺ SnCl ₂ (SPy)	2.02	8 ^h
	tbp	MeSnCl ₂ (SPyN)	2.45	8 ^h
		Bu ⁺ SnCl ₃ [Ni(salphen)]	1.48	12
		Bu ⁺ SnCl ₃ (dmpe)	2.08	13
	pbp	(<i>p</i> -Cl-C ₆ H ₄)Sn(SPy) ₃	1.92	8 ^h
		MeSn(SPy) ₃	2.23	8 ^h
		Na ₃ [Ph ₂ Sn(SCH ₂ CH ₂ SO ₃) ₂].2H ₂ O	1.44	14
	(cis-R ₂) tbp	Me ₂ SnCl[(η^1 -C ₅ H ₅) ₂ Mo(H)]	3.17	6
		Ph ₂ Sn(glyala)	2.21	15
		(Et ₃ SnCl) ₂ ·(H ₂ bim)	3.88	16
	(trans-R ₂) tbp	[Me ₂ Sn(nicO)] ₂ O	2.15	17
		Bu ⁺ Sn(glulac)	4.16	18
		Ph ₂ SnCl ₂ ·(H ₂ safth)	1.76	19
	(cis-R ₂) oct	Bu ⁺ Sn[(O ₂ CCH ₃) ₂ ·(chda)]	2.58	20
		Ph ₂ Sn(SPy) ₂	2.31	21
		[Me ₂ Sn(SO ₃ F)] ₂ [Pt(SO ₃ F) ₆]	5.70	22
	pbp	Ph ₂ Sn(dapa)	3.12	23
		Bu ⁺ Sn[(O ₂ CC ₆ H ₃ -2,6(OH) ₂] ₂	4.66	24
		Ph ₃ Sn(aet)	1.19	25
	(eq-R ₃) tbp	[(Cy ₃ Sn)] ₂ (pdaa)	3.21	26
		[(<i>p</i> -tolyl) ₃ Sn(pyt)](S ₂ CNMe ₂)	2.47	27
		(Me ₃ Sn) ₂ SO ₄ ·2H ₂ O	4.11	28
	(fac-R ₃) tbp	(<i>p</i> -tolyl) ₃ Sn[ON(Ph)COPh]	1.82	29
		Ph ₃ SnO ₂ CC ₆ H ₅	2.55	30
		Bu ⁺ Sn(paba)	2.99	31
	sp	[(<i>p</i> -tolyl) ₃ Sn(diphosO ₂)](Ph ₄ B)	4.08	29
		(C ₆ H ₅ CH ₂) ₃ Sn(SPyO)	1.99	32
		Ar ₄ Sn	0.00	33
R ₄ Sn ^{IV}	tet	Bu ⁺ Sn(btz)	1.20	34
		MeSn(CH ₂ CH ₂ CH ₂) ₃ N	0.60	35
	oct	Ph ₂ Snpyt ₂	0.73	36

^aTin environment: tet=tetrahedral; sp=square pyramidal; pyr=pyramidal; tbp=trigonal bipyramidal; oct=octahedral; pbp=pentagonal bipyramidal; eq=equatorial; fac=facial; mer=meridional. Note that the assumed *trans*-R₂ tbp structures violate the rule by Muetterties and Schunn [Muetterties, E.L. and Schunn, R.A. (1966) *Quart. Rev. Chem. Soc., London*, **20**, 245].

^bR=organic radical; Ar=aryl; Me=methyl; Et=ethyl; Bu⁺=*n*-butyl; Ph=phenyl; Cy=cyclohexyl; Py=pyridyl; pyt=3-(2-pyridyl)-2-thienyl. Ligands: H₂Thor=2-thio-orotic acid; H₂saldph=*N,N'*-(4,5-dimethyl-1,2-phenylene)bis(salicylideneimine); HSPyN=2-mercaptopyrimidine; HSPy=2-mercaptopyridine; HSPyO=2-mercaptopyridine *N*-oxide; Pc=phthalocyanine; Hdaptsc=2,6-diacetylpyridinebis(thiosemicarbazone); H₂salphen=[*N,N'*-o-

phenylenebis(salicylideneimine)]; dmpe = 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane; H₂glyala = glycylalanine; H₂bim = 2,2'-biimidazole; HnicO = nicotinic acid *N*-oxide; glulac = D-gluconic acid δ -lactone; H₃saft = salicylaldehyde-2-furanthiocarboxylhydrazone; chda = *o*-cyclohexadiamine; H₂dapa = [2,6-diacetylpyridine-bis(2-aminobenzoylhydrazone)]; Haet = aminoethanethiol; H₂pdaa = 1,3-bis(2'-carboxyphenylamine)propane; Hpaba = *p*-aminobenzoic acid; diphosO₂ = Ph₂P(O)CH₂CH₂P(O)Ph₂; Hbtz = benzothiazole.

^cNuclear quadrupole splitting, referred to solid state absorbers at liquid N₂ temperature, unless otherwise stated in the cited references. Low and high ΔE values are generally reported for each class, when available, taken from literature data 1986–1995.

^dTrigonal bipyramidal with the non-bonding pair of electrons of the tin(II) atom pointing along the axial direction of a distorted pseudo-six-coordinated geometry.

^ePseudo-seven-coordinated compounds containing octahedral SnX₆ in which the tin(II) environment tends to distort in order to accommodate directional non-bonding electron pairs.

^fDistorted pentagonal bipyramidal geometry, with the tin(II) atom occupying an apical position.

^gPyramidal environment with the non-bonding electron pair stereochemically active.

^h ΔE_{av} in the temperature ranges 77.3–148.5 K (Sn^{IV}) and 77.3–155 K (MeSn^{IV}); R. Schmiedgen *et al.*, personal communication.

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the nature of the Sn environment, is then effected by the determination of the functions $\delta/[\psi(0)_s]_a$ as well as δ /parameter related to $[\psi(0)_s]_a$.

The field has been widely commented and reviewed by Flinn [26], Bancroft and Platt [17] and Parish [18, 19] to which the reader is referred.

Summarizing the results of a large series of investigations, the ^{119}Sn δ -parameters were found to correlate to the following functions:

- Sn^0 , Sn^{II} , Sn^{IV} , $\text{R}_n\text{Sn}^{\text{IV}}$:
 - $5s$ Sn electron density calculated by a self-consistent molecular orbital method [5]; a unique function is obtained for SnX_4 ($\text{X}=\text{H}$, Me, Cl, Br, I); Snhal_6^{2-} ($\text{hal}=\text{F}$, Cl, Br, I); MeSnH_3 ; Me_2SnH_2 ; Me_2SnCl_2 ; Me_3Snhal ($\text{hal}=\text{Cl}$, Br, I). An analogous function, including Sn^0 and Sn^{II} derivatives, has been reported [11].
 - The average Pauling electronegativity, χ_p , of atoms bound to Sn, for a large selection of inorganic and organometallic Sn^{IV} derivatives, and Sn metal; two distinct correlations are detected [26].
 - The number of $5s$ and $5p$ Sn electrons as functions of δ and $5s$ electron density, for a series of Sn^{II} and Sn^{IV} derivatives, and Sn^0 [11, 26].
- Sn^{IV} :
 - χ_p , or χ_M (i.e. the average Mulliken electronegativity of bound atoms) for Snhal_4 ($\text{hal}=\text{F}$, Cl, Br, I [11, 73]; $\text{hal}=\text{Cl}$, Br, I [8, 17, 38]).
 - $\chi_{p,M}$ for Snhal_6^{2-} ($\text{hal}=\text{Cl}$, Br, I) and $\text{SnX}_4\text{Y}_2^{2-}$ (X , $\text{Y}=\text{F}$, Cl, Br, I [6, 8, 17, 38, 73]); χ_M for SnX_4 , SnX_5^- , LSnX_4 [74]; χ_M for $\text{L}_n\text{SnX}_{6-n}$ [74] ($\text{L}=\text{ligands}$ with O, N, S, P coordinating atoms).
 - Charge on Sn for Snhal_4 ($\text{hal}=\text{Cl}$, Br, I), Snhal_6^{2-} ($\text{hal}=\text{Cl}$, Br, I), $\text{SnX}_4\text{Y}_2^{2-}$ (X , $\text{Y}=\text{F}$, Cl, Br, I) [20].
- Sn^{II} :
 - The nuclear quadrupole splitting, ΔE , for a large selection of salts, complexes Snhal_3 , and other derivatives [26]; for SnX_3^- complexes ($\text{X}=\text{F}^-$, Cl^- , Br^- , SCN^- , HPO_3^{2-} , HCO_3^- , OH^- , CH_3COO^- , $\text{ClCH}_2\text{COO}^-$) [5].
 - χ_M for $\text{Sn}(\text{XYZ})$ (X , Y , $\text{Z}=\text{F}$, Cl, Br, I) [8, 18]; three independent correlations are obtained as function of the cation Bu_4N^+ , Ph_4As^+ , Et_4N^+ [8].
 - χ for Snhal_2 ($\text{hal}=\text{F}$, Cl, Br, I) [73] (irregular trend).
- $\text{R}_n\text{Sn}^{\text{IV}}$:
 - $\chi_{p,M}$; individual correlations are obtained for the series:
 - MeSnhal_3 ($\text{hal}_3=\text{F}_3$, FCl_2) [26].
 - EtSnhal_3 ($\text{hal}=\text{Cl}$, Br, I) [26].
 - $\text{Bu}^n\text{SnX}_n\text{Y}_{5-n}^{2-}$ (X , $\text{Y}=\text{F}$, Cl, Br) [73].

- $\text{Me}_2\text{Snhal}_2$ ($\text{hal}_2 = \text{F}_2, \text{FCl}, \text{Cl}_2, \text{Br}_2$) [26, 73].
- $\text{Et}_2\text{Snhal}_2$ ($\text{hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [26].
- $\text{Me}_2\text{Snhal}_4^{2-}$ ($\text{hal} = \text{F}, \text{Cl}, \text{Br}$) [17].
- $\text{Ph}_2\text{Snhal}_2$ ($\text{hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [73].
- Me_3Snhal ($\text{hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [17, 2⁶, 73].
- Ph_3Snhal ($\text{hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [73].

The original references, as well as further correlations concerning δ -parameters of Sn derivatives, are reported in the treatises and reviews quoted in the preceding text.

Subsequent work has been largely concerned with the evaluation of the partial electric charge on tin, Q_{Sn} , in series of congeneric salts and complexes, to be correlated with the respective δ -parameters. The estimate of Q_{Sn} is based upon the procedure of orbital electronegativity equalization on bond formation, by Jaffé and coworkers [75–77] and the treatment by Huheey [78]. The empirical procedure by Jolly, Perry and Avanzino [79–81] ‘incomplete orbital electronegativity equalization’ is employed in the calculations. The obtained values of Q_{Sn} agree, in principle, with data extracted from Dirac–Slater self-consistent field (SCF) and molecular orbital (MO) [82], as well as MNDO (modified neglect of diatomic overlap) [83] calculations, at least as far as the obtained trends are concerned. By this procedure, individual δ/Q_{Sn} correlations have been established for a large selection of classes of congeneric compounds, as outlined in the following:

- Six-coordinated Sn, octahedral structures: complexes of Snhal_4 , RSnCl_3 , R_2SnCl_2 , Me_3SnCl , with mono- and bidentate ligands coordinating P, O and N atoms [84, 85].
- Five-coordinated Sn, trigonal bipyramidal structure: species $(\text{R}_3\text{SnX})_n$ (X =axially bridging atoms or groups); complexes R_3Snhal_2 , $\text{R}_3\text{SnX}(\text{L})$, R_3SnL_2^+ , R_2SnL_3 , R_2Snhal_3 , $\text{Ph}_2\text{SnCl}_2(\text{L})$, $\text{R}_2\text{SnX}(\text{L}_2)$, $\text{RSnCl}(\text{L}_3)$, $\text{Snhal}_2(\text{L}_3)$; ($\text{X}=\text{hal}, \text{NCS}, \text{NCO}, \text{OH}, \text{OR}, \text{CN}, \text{N}_3$; $\text{L}=\text{O}, \text{N}, \text{S}$ donor atoms from a variety of ligands [86–90]).
- Four-coordinated Sn, tetrahedral species: calculations of Q_{Sn} for Alk_3SnI , Cy_3SnBr , $\text{R}_2\text{Sn}(\text{SR}')_2$, $\text{R}_3\text{Sn}(\text{SR}')_2$ [87, 91]).

The correlations obtained are exemplified in Figure 14.9. It is concluded that the rationalization of δ -parameters, as discussed in the preceding text, identifies series of isostructural, congeneric derivatives, and may contribute to the assignment of structure to individual terms of the series. Further δ/Q_{Sn} correlations, concerning organotins interacting with biological and model molecules and systems, are mentioned in section 14.10.2.

Lastly, previous work on the rationalization of ^{119}Sn Mössbauer parameters δ by the correlation with the Sn $3d_{5/2}$ binding energy corrected for the Madelung potential, as extracted from X-ray photoelectron spectroscopy [73], has been extended to the study of a series of octahedral adducts

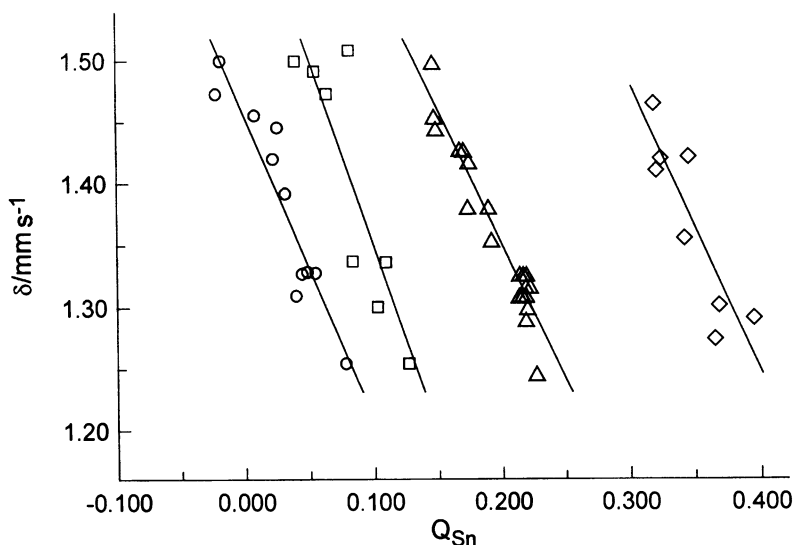


Figure 14.9 The correlation δ/Q_{Sn} (Mössbauer isomer shift vs. partial atomic charge on tin) for homologous series of compounds: (O) $[\text{R}_3\text{Snhal}_2]^-$; (□) $[\text{R}_2\text{Snhal}_3]^-$; (Δ) $(\text{R}_3\text{SnX}(\text{E}=\text{O}))$; (◇) $[\text{R}_3\text{Sn}(\text{E}=\text{O})_2]^+$; R = alkyl, aryl; hal = Cl, Br, I; X = Cl, Br, NCS; (E=O) are oxygen-coordinating groups from a series of ligands, E being C, P, As, S. Full lines are least square fits of data points; the related equations and correlation coefficients are: (O) $\delta = 1.44 - 2.64 Q_{\text{Sn}}$ ($r = 0.939$); (□) $\delta = 1.66 - 3.26 Q_{\text{Sn}}$ ($r = 0.876$); (Δ) $\delta = 1.81 - 2.37 Q_{\text{Sn}}$ ($r = 0.960$); (◇) $\delta = 2.24 - 2.54 Q_{\text{Sn}}$ ($r = 0.877$) (Adapted from Ref. 88.)

$\text{SnCl}_4(\text{P}, \text{P})$, $\text{R}_3\text{SnCl}_3(\text{P}, \text{P})$ and $\text{Ph}_2\text{SnCl}_2(\text{P}, \text{P})$ (P,P are donor atoms from 1,2-bis(diphenylphosphino)ethane; R = Me, Buⁿ, Octⁿ, Ph) [92].

14.7.2 Nuclear quadrupole splitting

The electric field gradient tensor. According to eqn 14.3, the nuclear quadrupole splitting ΔE arises from the interaction of the external (with respect to the nucleus) electric field gradient, EFG, with the nuclear quadrupole moment. Information may then be obtained about the EFG, and consequently about the charge distribution in the environment of the nucleus. To this purpose, a relatively detailed treatment of the EFG properties and characteristics seems to be opportune in the present context, especially in view of the treatment below (see The additivity model), a semi-empirical procedure for structural assignments from ΔE data. The approach by Travis [43] is essentially followed here, also taking into account further treatments reported in the literature [5–7, 10, 11, 17–19, 36, 38, 44, 73, 93].

The electrical charges external to the Mössbauer nucleus, localized in bonding ligand atoms, are considered as point charges, according to the crystal field theory model. These charges determine the 'ligand contribution'

to the EFG tensor; besides, they perturb the wave function of the Mössbauer (central) atom, and the electrons in these resulting functions give the 'valence contribution' to the EFG [43]. Both contributions may be rationalized by the procedure described in the following.

The 'ligand contribution' of one point charge q at (x, y, z) , at distance $r = (x^2 + y^2 + z^2)^{1/2}$ from the Mössbauer nucleus (the latter at the origin of the Cartesian axes), is given by [43]:

- the potential at the Mössbauer nucleus:

$$V = q/r \quad (14.5)$$

- the negative gradient of this potential is the electric field at the nucleus:

$$E_x = -\partial V/\partial x = qxr^{-3}; \quad E_y = -\partial V/\partial y = qyr^{-3}; \quad E_z = -\partial V/\partial z = qzr^{-3} \quad (14.6)$$

- the gradient of the electric field at the nucleus is given by the 3×3 tensor:

$$\text{EFG} = \begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix} \quad (14.7)$$

where $V_{ab} = \partial^2 V / \partial a \partial b$

The components of the EFG tensor in polar coordinates are as follows for its 'standard forms' [43]:

$$\begin{aligned} V_{xx} &= q(3\sin^2\theta\cos^2\phi - 1)r^{-3} \\ V_{yy} &= q(3\sin^2\theta\sin^2\phi - 1)r^{-3} \\ V_{zz} &= q(3\cos^2\theta - 1)r^{-3} \\ V_{xy} &= V_{yx} = V_{xz} = V_{zx} = V_{yz} = V_{zy} = 0 \end{aligned} \quad (14.8)$$

i.e. only the diagonal elements of the 3×3 tensor show non-zero values. Moreover, in the 'standard form' the diagonal elements are characterized by

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}| \quad (14.9)$$

x, y, z being now termed 'the principal axes of the EFG tensor' [43]. Then, two independent parameters describe the diagonal elements of the EFG gradient in the 'standard form': V_{zz} and the asymmetry parameter η [43]:

$$\eta = (|V_{xx} - V_{yy}|)/V_{zz} \quad (14.10)$$

From eqn 14.9 it follows that η may assume values in the range 0–1 [43].

Any individual ligand atom, metal-bound in salts and complexes, is described as a point charge q_k at a distance r_k from the metal, originating a specific EFG tensor (eqn 14.7). The total EFG tensor, due to all ligand point charges in the environment of the Mössbauer nucleus, consists of the sum of all tensors. Expressions are tabulated for total $V_{\alpha\alpha}$, based upon eqn 14.8, for tetrahedral, trigonal bipyramidal and octahedral metal environments [6, 17–19, 43, 73].

Combined quadrupole and magnetic interactions. The sign of V_{zz} (and consequently of ΔE), and the η value (eqn 14.10) cannot be determined from ΔE obtained by experimental spectra, such as in Figure 14.2 [93]; only for $\eta=0$, the quadrupole splitting consists of a measure of V_{zz} , in the case of nuclei with spin $3/2$ such as ^{119}Sn , but the sign is not measured [93].

These parameters may be determined by the application of an external magnetic field to the absorber sample (consisting, for example, of a powdered solid compound), which splits the degeneracy of spin $3/2$ nuclei [93–96]. For example, in the case of an absorber compound with $\eta=0$ to which a magnetic field parallel to the γ -ray beam is applied, nuclear energy levels are split as shown in Figure 14.10, and eight absorption bands may occur [93]: from the experimental spectrum, and its computer fitting, the sign of V_{zz} , and then of ΔE , is obtained.

In the case of the application of strong magnetic fields, as well as for $\eta \neq 0$, the fitting of the experimental spectra is effected by employing a computer program which diagonalizes the 4×4 spin $3/2$ Hamiltonian matrix (sections 14.4 and 14.10.1) yielding (sign) ΔE and the value of η [93].

An example of the application of this treatment to tin derivatives is shown in Figure 14.11. The doublet spectrum (a) of $(\text{CH}_3)_2\text{SnF}_2$ is shifted to (b) in a transverse magnetic field applied to the absorber; the computed Mössbauer–Zeeman spectrum (b) is obtained by employing the parameters $\Delta E = +4.65 \text{ mm s}^{-1}$, $(-V_{zz}, \eta = 0.00 \text{ } (V_{xx} = V_{yy}))$. These data imply the occurrence of the tin environment, as well as the attribution of the axes of EFG at the Sn nucleus, reported in Figure 14.12. The structure thus extracted corresponds fully to that determined by X-ray diffractometry, providing evidence of the occurrence of a solid state bidimensional polymer with bridging F atoms [100].

Studies of ^{119}Sn Mössbauer–Zeeman spectroscopy on a series of tin derivatives have been reviewed, the determined signs of ΔE being tabulated [6, 8, 17, 20, 94].

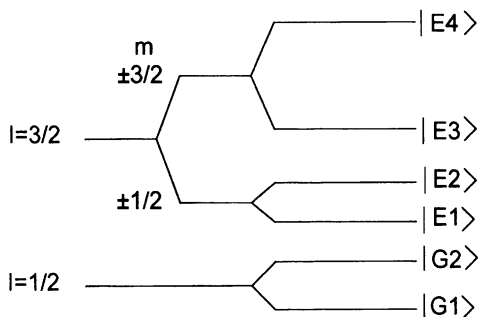


Figure 14.10 Combined quadrupole and magnetic interaction: first-order approximation nuclear energy level diagram. $|G\rangle$ and $|E\rangle$ are the (approximate) eigenvectors obtained from the ground state and excited state Hamiltonian matrices, respectively. (Adapted from Ref. 93.

See also Refs 2, 5, 8, 10, 11, 18, 20, 36, 94, 96, 97.)

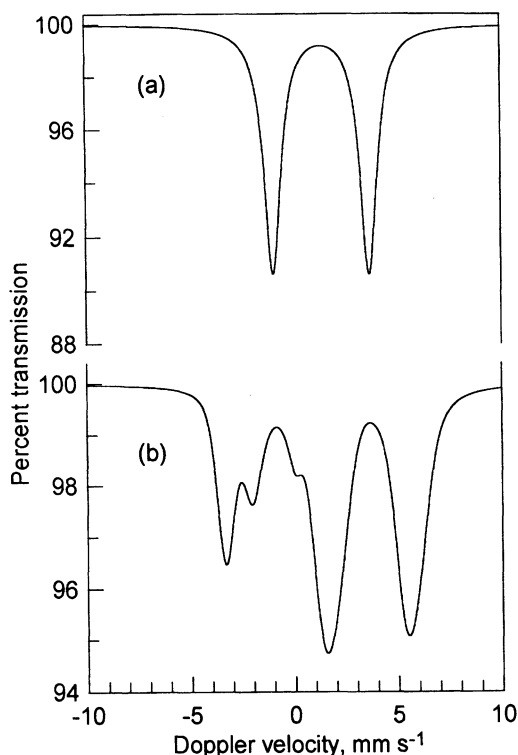


Figure 14.11 ^{119}Sn Mössbauer spectra of $(\text{CH}_3)_2\text{SnF}_2$: (a) $T=77.3$ K, measured on powdered sample without applied field; (b) $T=4.2$ K in a magnetic field of 4 T perpendicular to the γ -ray direction. Spectral simulation by the computer programs described in section 14.4, employing the parameters [98] $\delta=1.34$; $\Delta E=4.65$; $\Gamma=1.00\text{ mm s}^{-1}$ for spectrum (a); $\Delta E=+4.65$, $\eta=0.00$ for spectrum (b) [99]. The simulated spectrum (b) corresponds to the experimental spectrum measured at 4.2 K in a magnetic field of 4 T perpendicular to the γ -ray beam [99].

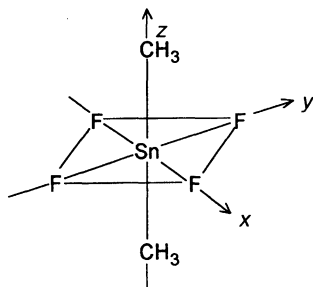


Figure 14.12 The environment of tin atoms in the bidimensional polymer, $(\text{CH}_3)_2\text{SnF}_2$, with bridging F atoms. Structure assigned by ^{119}Sn Mössbauer–Zeeman spectroscopy, in accordance with structural data from X-ray diffractometry [100]. x , y , z are the assigned directions of the principal components of the EFG tensor.

The additivity model. Once the sign of ΔE (eqn 14.3) and the value of η (eqn 14.10) are experimentally obtained by Mössbauer–Zeeman spectra, a semi-empirical procedure may be employed in order to extract structural information from ΔE parameters. The so-called additivity model is employed for this purpose. It has been widely described, together with the related procedures, by Bancroft and Platt [6, 17] and Parish [19], based on the detailed treatment by Clark *et al.* [101, 102]. A brief survey is reported here, essentially following the treatment by Bancroft and Platt [17].

The additivity model defines the quadrupole splitting as the sum of contributions by each ligand bound to the Mössbauer atom, being a function of the ligand-to-metal bonds as well as of the related structure of the metal environment. The model may be applied to Mössbauer atoms where the metal electrons, not involved in bonding, do not influence the EFG (e.g. Fe^{II} , t_{2g}^6 , and Sn^{IV} , $4d^{10}$; not Sn^{II} , due to the doublet $5s^2$).

The diagonal components of the individual EFG tensor in the standard form, eqn 14.8, due to a single point charge, are defined in ΔE units, i.e. the qr^{-3} quantity is substituted by a ‘partial quadrupole splitting’, p.q.s.:

$$\text{p.q.s.} = \frac{1}{2}e^2 |Q| (qr^{-3}) \quad (14.11)$$

Individual p.q.s. values are then calculated by eqns 14.3 and 14.8 for any individual ligand atom in e.g. tetrahedral, trigonal bipyramidal (axial and equatorial) and octahedral Sn^{IV} as well as $\text{R}_n\text{Sn}^{\text{IV}}$ salts and complexes ($n=1-3$), with known molecular structure, and known (sign) ΔE and value of η from Mössbauer–Zeeman spectroscopy.

Unknown structures may now be assigned by the reverse procedure: i.e. ΔE values are experimentally determined for given compounds, and ΔE values are calculated for possible structures by employing the related p.q.s. values, by eqns 14.3 and 14.8. The assumed structure would be considered to be the actual structure for $|\Delta E_{\text{exp}} - \Delta E_{\text{calcd}}| \leq \pm 0.4 \text{ mm s}^{-1}$ [102].

A large collection of p.q.s. data is reported in the literature [17, 19, 73, 102–104] and the results of structural attributions by this procedure are widely tabulated [17–19, 102–104].

The calculation of ΔE and estimates of p.q.s. referred to above generally concern regular tetrahedral, trigonal bipyramidal and octahedral geometries; small distortions are generally ignored [102]. Heavily distorted systems are treated in the following way [19, 105]. In the case of $\text{R}_2\text{Sn}^{\text{IV}}$ derivatives, where ligand atoms other than C are highly electronegative atoms, such as halides, nitrogen and oxygen, the EFG is considered to be determined essentially by the covalent Sn–C bonds, according to the related p.q.s. magnitudes. Under these conditions, point charge-additive model calculations are effected by employing only p.q.s. values for the organic radicals bound to Sn, and ignoring the contributions by the remaining ligands [19, 105]. The following equation is employed [19].

$$\Delta E_{\text{calcd}} = -4[R][1 - (3/4)\sin^2\theta]^{1/2} \quad (14.12)$$

where $[R]$ are the p.q.s. data related to the given structure and θ is the C–Sn–C angle. A satisfactory $\Delta E/[R]$ vs. θ function is obtained [19], from which C–Sn–C angles, θ , may be approximately estimated by interpolation. Analogous treatments may be employed for R_3SnX derivatives to estimate C–Sn–X angles [19, 106]. The approach described above essentially corresponds to the treatment by Travis [43] who assumes the EFG to be due to two point charges A and B in a MAB unit, where M is the central metal atom.

Applications of these concepts and procedures are described in section 14.10. It is worth noting that the structural information thus obtained concerns only the geometry of the bonding environment of tin in di- and triorganotin(IV) derivatives, which may complement the straightforward and unequivocal structural information extracted from X-ray diffractometry on crystalline solids, as well as from multidimensional NMR in solution phases.

14.7.3 Theoretical treatment of ^{119}Sn Mössbauer spectra

Earlier molecular orbital approaches were concerned with the representation of the valence contribution of a ligand to EFG in terms of the effect on the population of the atomic orbitals of the Mössbauer metal [17]. A simple, but general, molecular orbital model for additive EFG has been proposed, and applied to organotin(IV) compounds [101, 102]. Recent theoretical studies are due to Grodzicki and coworkers concerning semiempirical molecular orbital calculations and their correlation to the experimental hyperfine parameters δ and ΔE [107]. In particular, electronic charge densities $\rho(0)$ and electric field gradients V_{zz} at the ^{119}Sn nucleus were calculated essentially by the self-consistent charge SCC- $X\alpha$ -MO method, and correlations of $\rho(0)$ with δ and V_{zz} vs ΔE were extracted for a series of Sn^{II} and Sn^{IV} derivatives [108, 109]. Analogous correlations have been found for organotin(IV) compounds, MO calculations of $\rho(0)$ and EFG being carried out by STO-3G, MINI-4 and DZ programs [110]. EFG for Sn^{II} and Sn^{IV} systems have been calculated by the DV-LCAO procedure, and the nuclear quadrupole moment Q has been determined [111].

14.8 Dynamics of Mössbauer nuclei

The study of the dynamics of nuclei (e.g. ^{57}Fe and ^{119}Sn), and consequently of molecular fragments in the neighborhood of these atoms by Mössbauer spectroscopy, is essentially based on the established correlation between the Mössbauer recoilless fraction f (the Debye–Waller–Mössbauer or Lamb–Mössbauer factor) and the mean square displacement $\langle x^2 \rangle$ of nuclei, or connected masses (eqn 14.1). The related theory, which is based upon the

classical solid state physics of lattice vibrations, on the assumption of the Debye model, is detailed [1, 2], as well as summarized [8, 36] or sketched [5, 7, 10, 11], in a number of treatises and reviews.

The dynamics from the Mössbauer effect are treated extensively by Kolk [112], as well as by Herber [113] and Bauminger and Nowik [114]. A number of review articles in the context of ^{119}Sn dynamics have been published [e.g. 115, 116], also, some concern fingerprint applications to structural features [19, 20].

The usual procedures in the study of, for example, ^{119}Sn dynamics, consist of the determination of the temperature dependence of the total area, A_{tot} , under the resonant peaks, which is correlated to the corresponding function concerning the Lamb–Mössbauer factor, f_a ; these are summarized in the following, essentially according to Herber's notation [113].

In the high temperature limit ($T \geq \vartheta_D/2$), in the Debye approximation, eqn 14.13 holds [113]:

$$f_a = \exp(-3E_\gamma^2 T / Mc^2 K \vartheta_D^2) \quad (14.13)$$

where E_γ is the energy of the Mössbauer transition; M is the effective vibrating mass, EVM; c is the velocity of light; K is the Boltzmann constant and ϑ_D is the Debye temperature. Accounting for the relationship between A_{tot} and f_a , for a 'thin' absorber, eqn 14.14 is obtained [113]:

$$\frac{d \ln A_{\text{tot}}}{dT} = \frac{d \ln f_a}{dT} = \frac{-3E_\gamma^2}{Mc^2 K \vartheta_D^2} \quad (14.14)$$

from which 'relative' values [117], f_a^{rel} , of $f_a(T)$ are estimated from eqn 14.13.

Mean square displacements of the ^{119}Sn nucleus, $\langle x^2 \rangle(T)$, are then calculated by [113]:

$$f_a = \exp(-k^2 \langle x^2 \rangle) \quad (14.15)$$

k being the wave vector of γ -rays.

Debye temperatures are calculated by eqn 14.14, assumed to be independent of T (which, on the other hand, would not hold in the high T range [36]); then, Debye cut-off frequencies ν_D are obtained [36]:

$$\nu_D = \frac{K \vartheta_D}{h} \quad (14.16)$$

h being the Planck constant and K the Boltzmann constant.

'Absolute' values of f_a , i.e. f_a^{abs} , are instead estimated as follows. The Lamb–Mössbauer factor of the source, f_s , is obtained from spectra, at 77.3 K, of white β -tin, 0.1 mm thickness. Its effective thickness, t_i , is defined by [118, 119]:

$$t_i = (\pi/2) \Gamma_{\text{nat}} N \sigma_0 f_a \quad (14.17)$$

where Γ_{nat} is the ^{119}Sn natural line width, N is the number of absorber reso-

nant atoms per square centimetre and σ_0 is the resonant cross-section of ^{119}Sn ; published f_a data are employed [120]. From t_i , on the assumption of resonant Lorentzian lines, the corresponding saturation functions $L(t_i)$ [119] are estimated from tabulated data [121], and f_s is calculated by [118, 119]:

$$f_s = \frac{A}{(\pi/2)\Gamma_{\text{nat}}L(t_i)} \quad (14.18)$$

where A is the experimental Mössbauer area of the β -tin absorber.

The reverse procedure gives f_a^{abs} . In fact, for absorber samples consisting of e.g. tin(IV) or organotin(IV) derivatives, $L(t_i)$ are calculated from the areas (A_1, A_2) corresponding to each peak of the doublet (for two-peak spectra), by eqn 14.18. From $L(t_1)$ and $L(t_2)$ the values of t_1 and t_2 are estimated by interpolation [119], and f_a^{abs} calculated by eqn 14.19 [118].

$$f_a^{\text{abs}} = \frac{t_1 + t_2}{(\pi/2)\Gamma_{\text{nat}}\sigma_0 N} \quad (14.19)$$

The reliability of these f_a^{abs} data is due to their being obtained from area ratios, which implies the cancelling out of eventual experimental failures in the determination of the individual areas.

From $f_a^{\text{abs}}(T)$, functions $\langle x^2 \rangle(T)$ and parameters ϑ_D and ν_D are then calculated by eqns 14.13, 14.15 and 14.16. These data have been also applied to empirical estimates of the extent of intermolecular interaction in a series of tin compounds (mainly organotins) by fingerprinting, based upon the following criteria:

1. the temperature dependence of $\langle x^2 \rangle$ [122];
2. the magnitude of ϑ_D , and then of $M\vartheta_D^2$ (the 'parameter of intermolecular interaction', M , being the molecular mass) [123];
3. the slope of functions $\ln A(T)$ [and, consequently, of $\ln f_a^{\text{rel,abs}}(T)$];
4. limited $\langle x^2 \rangle$ increments with increasing T , high ϑ_D (and $M\vartheta_D^2$) values, and low slopes $d \ln f_a^{\text{rel,abs}}/dT$ characterize solid state 'polymeric' materials.

Approximate fingerprint criteria are as follows:

Organotin(IV) monomers and monodimensional polymers are distinguished from bi- and tridimensional polymers by the borderline $\langle x^2 \rangle \sim 0.8 \times 10^{-2}$ (77.3 K); 2.0×10^{-2} (200 K); 2.8×10^{-2} (280 K), \AA^2 . Mainly for organotin(IV) derivatives, $\vartheta_D = 21.6$ –68.5 K for monomeric species and 58.6–105.7 K for polymers [123].

Criterion (3) above, described here in the following, is by far the most commonly employed one. To date, a considerable number of slopes $d(\ln A)/dT$ for inorganic and organometallic tin derivatives have been reported [19, 20, 124–126]. The most reliable ordering seems to consist of the selection of data for congeneric series of compounds, as far as the nature of the radicals bound to the metal [124] (alkyl or aryl), and their number [125,

126] are concerned, as shown in Figure 14.13. Classes of phenyl and cyclohexyltin polymers have been identified by Molloy and Quill [124] on the basis of slope data and of known structures. The correlation $d(\ln A)/dT$ vs. $1/EVM$ [19] (where EVM is the effective vibrating mass as defined by Hazony and Herber [131]) allowed the degree of polymerization to be established for members of a congeneric series [125]. In any case, caution must be exerted in the application of these procedures, due to the generally wide borderline data zone which occurs in any series of congeneric derivatives [19, 20, 124–126] (Figure 14.13).

Applications of these concepts and procedures are contained in section 14.10.

14.9 Applications to materials, and environmental interactions

14.9.1 Tin in polymers, glasses and paints

In the context of the industrial uses of tin chemicals [132], addition to polymeric materials [mainly with the aim of thermal stabilization of poly(vinyl

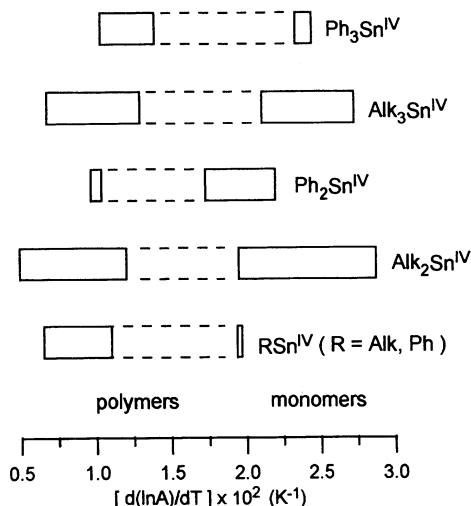


Figure 14.13 Fingerprint estimates of the extent of intermolecular interaction in organotin(IV) derivatives, from ^{119}Sn Mössbauer dynamics of the tin nuclei determined through the slopes of functions: area under the resonant peaks, A , vs. temperature (see text). Border zones (dashed): polymers and monomers. (Limiting slope values are taken from Refs 19 ($\text{Alk}_3\text{Sn}^{\text{IV}}$); 127 ($\text{Alk}_3\text{Sn}^{\text{IV}}$); 128 ($\text{Alk}_3\text{Sn}^{\text{IV}}$); 129 ($\text{Alk}_3\text{Sn}^{\text{IV}}$, $\text{Ph}_3\text{Sn}^{\text{IV}}$, $\text{Ph}_2\text{Sn}^{\text{IV}}$); data calculated from the reported $d(\ln A)/dT$ values); 124 ($\text{Ph}_3\text{Sn}^{\text{IV}}$ and $\text{Ph}_2\text{Sn}^{\text{IV}}$); 130 ($\text{Ph}_3\text{Sn}^{\text{IV}}$); 125 ($\text{Alk}_2\text{Sn}^{\text{IV}}$), and 126 (RSn^{IV}). Slope zones include data from Refs 19, 20, 124–126; data for additional 87 tin sites, published in the period 1967–1995, not previously reviewed (L. Pellerito *et al.*, in preparation).

chloride) (PVC) [133] and as antifouling agents for elastomeric matrixes], as well as to glasses, has been reported. Recent work will be commented upon briefly here; earlier work in these fields has been amply treated by Blunden *et al.* [132]. Mössbauer parameters are cited by Parish [19].

In these systems, ^{119}Sn Mössbauer spectroscopy is employed as an analytical technique. By fingerprinting, rapid and non-destructive identification of the tin species is effected [134] (in qualitative analysis, any individual compound gives essentially a characteristic spectrum, and mixtures of compounds result in complex signals); moreover, compounds are quantitatively estimated by the areas under the resonant peaks [134, 135]. Variable temperature Mössbauer spectroscopy is employed in order to distinguish species characterized by nearly corresponding spectra at low temperature [135]; this procedure has recently been applied to the study of SnCl_4 and Bu_3SnCl_2 dispersed in PVC, information being obtained on the extent of binding to the polymer matrix, which appears to be larger for SnCl_4 [136]. Further work concerns the speciation of Bu_3SnCl_2 dispersed in PVC, the occurrence of a dimeric species with five-coordinated tin being assumed by a point-charge model treatment of the ^{119}Sn Mössbauer parameter nuclear quadrupole splitting [137]. Moreover, thermal degradation of PVC treated with the stabilizers Oct_2Sn - and Bu_3Sn -bis(isooctylthioglycolate), as well as with Bu_3Sn -bis(isooctylmaleate), R_2SnL_2 , produces the R_2SnCl species [138], while γ -irradiation of the systems above yields SnCl_4 as the final degradation product [139]; Alk_2Sn -dilaurates and bis-ethylcysteineates are thermally degraded to $\text{Alk}_2\text{SnCl}_2$, while Sn(II) derivatives yield SnCl_4 and SnO_2 [140]. Tin(IV)-molybdenum oxidic systems have been shown to act as flame retardants and smoke suppressants in rigid PVC, yielding SnCl_2 , SnO and β -tin upon thermal degradation and combustion, according to ^{119}Sn Mössbauer studies [141].

Antifouling organotins encapsulated into elastomers, such as neoprene, as well as natural rubbers, have been employed to protect underwater installations, such as sonars, from fouling. Using ^{119}Sn Mössbauer spectroscopy, as well as by other techniques, it has been determined that $(\text{Bu}_3\text{Sn})_2\text{O}$ impregnated in neoprene yields Bu_3SnCl and Bu_3Sn stearate, as well as Bu_3Sn distearate, while in natural rubbers Bu_3Sn stearate and $(\text{Bu}_3\text{Sn})_2\text{S}$ would occur [142]. Further series of $\text{Bu}_3\text{Sn}^{\text{IV}}$ toxicants in neoprene gave evidence for the formation of Bu_3SnCl together with Bu_3Sn stearate and Bu_3Sn distearate [143, 144]. The degradation of Ph_3SnX toxicants ($\text{X} = \text{F}, \text{Cl}, \text{OAc}, \text{OSnPh}_3$) in neoprene yields Sn^{IV} derivatives [145, 146].

After exposure to a marine environment for a 2.5 year period, $(\text{Bu}_3\text{Sn})_2\text{O}$ in neoprene was degraded to SnO_2 through progressive hydrolysis and dealkylation, as determined by ^{119}Sn Mössbauer spectroscopy [147].

The employment of ^{57}Fe and ^{119}Sn Mössbauer spectroscopy in structural studies of glasses has been reviewed recently [148; see also 149]. Tin in glasses has been found to consist mainly of Sn^{II} in binary materials SiO_2 -Sn and in

float glass, while Sn^{IV} predominates in remelted specimens of $\text{SiO}_2\text{-SnO}$; the percentage $\text{Sn}^{\text{II}}/\text{Sn}^{\text{IV}}$ was estimated by the magnitude of 'f' factors calculated from variable temperature ^{119}Sn Mössbauer spectroscopy [150], the dynamics of tin nuclei being investigated [151]. Further work concerned arsenic-selenium-tin glasses [152], potassium-tin germanate glasses [153] and tin borate glasses [154], information being obtained on the tin valence state (Sn^{II} , Sn^{IV}), the relative percentage and the geometry of tin environments, as a function of sample preparation and treatment. Dynamics of ^{119}Sn nuclei, and the estimate of the parameter $M\theta_D^2$ (section 14.8) have been reported [153]. Float glass has also been investigated by conversion electron Mössbauer spectroscopy [155].

Recent work on antifouling paints has been concerned with triorganotin(IV) biocides incorporated into Hypalon (polyethylene with added chloro- and chlorosulphonyl derivatives) [156]. Using ^{119}Sn Mössbauer spectroscopy (and ^{119}Sn NMR), it was determined that $(\text{Bu}_3\text{Sn})_2\text{O}$ in Hypalon yields, *inter alia*, Bu_3SnCl ; besides, Ph_3SnCl and $\text{Ph}_3\text{Sn}(\text{OOCCH}_3)$ undergo dephenylation, while $\text{Bu}_3\text{Sn}(\text{OOCCH}_3)$, $(\text{Bu}_3\text{Sn})_2\text{CO}_3$ and $(\text{Ph}_3\text{Sn})_2\text{O}$ remain unchanged [156].

Lastly, it seems worthwhile to recall that the dynamic of tin nuclei embedded into polymeric materials, as investigated by variable temperature ^{119}Sn Mössbauer spectroscopy, does not give information on the degree of polymerization of the material, depending only upon the bonding situation at tin atoms. In fact, monomeric and polymeric di-*p*-tolyl-di-*p*-styryltin(IV) and tetra-*p*-styryltin(IV), as well as polymeric *p*-styryl- SnR_3 ($\text{R} = \text{Me}, \text{Ph}$) and 1,4-divinylbenzene- SnPh_2 , all show $\ln A_i/T$ functions (section 14.8) corresponding to those for Me_4Sn and Ph_4Sn [157, 158] (section 14.10.2).

14.9.2 Speciation analysis of organotin(IV) compounds in environmental systems

The study of the interaction of chemical organotin(IV) species with marine sediments is connected with the release of $\text{R}_n\text{Sn}^{\text{IV}}$ derivatives into the environment (including estuarine and marine water) due to their industrial uses [132, 159] (e.g. section 14.9.1). The argument has been recently reviewed [160]; in addition reviews have been published on environmental aspects of $\text{R}_n\text{Sn}^{\text{IV}}$ derivatives [161, 162].

Recent work has been concerned with the determination of the nature of $\text{Ph}_3\text{Sn}^{\text{IV}}$ compounds spiked to aquatic sediments (estuarine, anaerobic and aerobic) by ^{119}Sn Mössbauer spectroscopy, evidence being obtained about the persistence of Ph_3SnF and Ph_3SnCl , while Ph_3SnOH and $\text{Ph}_3\text{Sn}(\text{OOCCH}_3)$ were the source of $\text{Ph}_3\text{Sn}^{\text{IV}}$ which reacted with the sediments [163, 164]. Analogous studies have been carried out with $\text{Bu}_3\text{Sn}^{\text{IV}}$ derivatives [165].

14.10 Applications to tin chemistry

14.10.1 The structure of the tin environment as deduced from ^{119}Sn Mössbauer spectroscopy, and determined by X-ray diffractometry and NMR: $R_2\text{Sn}^{\text{IV}}$ dipeptides.

The procedures for structural assignments from $\Delta E_{\text{exp,calcd}}$ parameters, described in the section 14.7.2, are detailed here as exemplified by $R_2\text{Sn}$ -dipeptide complexes. The latter have been selected by considering the determinations of crystal and molecular structures by X-ray diffractometry of a large number of terms of the series (see references in Tables 14.3 and 14.4.), NMR structural studies in solution phases and numerous Mössbauer structural attributions both in the solid state and in solution. The interest, still persisting for this class of compounds, arises from their possible employment as antitumor drugs, although to date no component of the series has entered clinical practice [166]. Structures in the solution phase are necessary for QSAR (quantitative structure-activity relationship) attributions.

The general structure of the complexes, as extracted by X-ray crystallography (see references in Table 14.3), is shown in Figure 14.14. The related structural rationalization of ^{119}Sn Mössbauer parameters ΔE is effected as follows. The collective components of the diagonalized EFG tensor are [167]:

$$\begin{aligned} V_{xx} &= -\frac{1}{2}\{\text{R}\}^{\text{tbe}} + 2\{\text{N}_{\text{pept}}\}^{\text{tbe}} - \{\text{COO}\}^{\text{tba}} - \{\text{NH}_2\}^{\text{tba}} \\ V_{jj} &= +\frac{5}{2}\{\text{R}\}^{\text{tbe}} - \{\text{N}_{\text{pept}}\}^{\text{tbe}} - \{\text{COO}\}^{\text{tba}} - \{\text{NH}_2\}^{\text{tba}} \\ V_{kk} &= -2\{\text{R}\}^{\text{tbe}} - \{\text{N}_{\text{pept}}\}^{\text{tbe}} + 2\{\text{COO}\}^{\text{tba}} + 2\{\text{NH}_2\}^{\text{tba}} \end{aligned} \quad (14.20)$$

where $\{\text{L}\}^{\text{tbe,tba}}$ (L=ligand atom or ligand group) are p.q.s. values in $1/e^2 |Q| (qr^{-3})$ units (eqn 14.11), $V_{\alpha\alpha}$ being in the same units; tba=trigonal bipyramidal axial, tbe=trigonal bipyramidal equatorial; the axes x, j, k as shown in Figure 14.14. The values employed in the calculations of $V_{\alpha\alpha}$ are as follows: $\{\text{Alk}\}^{\text{tbe}} = -1.13 \text{ mm s}^{-1}$ [104], $\{\text{Ph}\}^{\text{tbe}} = -0.98 \text{ mm s}^{-1}$ [104], $\{\text{N}_{\text{pept}}\}^{\text{tbe}} = -0.30 \text{ mm s}^{-1}$ [167], $\{\text{NH}_2\}^{\text{tba}} = +0.01 \text{ mm s}^{-1}$ [167]. For $\{\text{COO}\}^{\text{tba}}$ the following two values have been employed: (1) $+0.075 \text{ mm s}^{-1}$, inherent to bridging carboxylate [167] groups involved in both coordination to Sn and hydrogen bonding to other groups, such as NH_2 [168], (2) -0.10 mm s^{-1} , for monodentate carboxylate [169] bound only to Sn.

With these data, the following calculated parameters are obtained for regular structures, such as those in Figure 14.14:

- $\{\text{COO}\}^{\text{tba}} = +0.075 \text{ mm s}^{-1}$:
 R=alkyl: $\Delta E_{\text{calcd}} = -3.08(5)$; $y=j$; $z=k$; $\eta = (|V_{xx} - V_{yy}|)/V_{zz} = 0.91$
 R=phenyl: $\Delta E_{\text{calcd}} = -2.70$; $y=j$; $z=k$; $\eta = 0.84$
- $\{\text{COO}\}^{\text{tba}} = -0.10 \text{ mm s}^{-1}$:
 R=alkyl: $\Delta E_{\text{calcd}} = +2.78$; $y=k$; $z=j$; $\eta = 0.95$
 R=phenyl: $\Delta E_{\text{calcd}} = -2.39$; $y=j$; $z=k$; $\eta = 0.98$

Table 14.3 Experimental values of C–Sn–C angles in crystalline five coordinated, trigonal bipyramidal R_2Sn^{IV} -dipeptide complexes (Figure 14.14) determined by X-ray diffractometry, as correlated to data extracted from the hyperfine parameters ^{119}Sn Mössbauer nuclear quadrupole splitting as well as calculated by the MNDO semi-empirical procedure

Compound ^a	C–Sn–C angles (°) from X-ray diffractometry	Ref.	δ^b (mm s ⁻¹)	ΔE_{exp}^c (mm s ⁻¹)	Ref.	C–Sn–C angles (°) estimated from:		MNDO calculations [Ref. 83]
						ΔE		
						(I) ^d	(II) ^d	
Me ₂ SnGlyMet	123.8	1	1.11	2.53	5	110.6	106.9	–
Me ₂ SnGlyGly	–	–	1.26	3.29	9	135.5	127.6	122.1
Me ₂ SnAlaHis	143.9	2	1.25	3.20	10	132.8	125.4	–
Me ₂ SnMetMet	132	2	1.16	2.94	10	125.0	118.7	–
Me ₂ SnTrpAla·CH ₃ OH	123.8	3	1.11	2.73	3	118.3	113.0	–
Et ₂ SnGlyTyr	131.4	4	1.26	2.87	4	122.9	116.9	–
Et ₂ SnGlyGly	–	–	1.18	2.69	4	116.9	111.9	117.6
Bu ₂ SnGlyVal	125.3	5	1.23	2.65	5	115.5	110.7	–
Bu ₂ SnGlyGly	–	–	1.35	3.19	9	132.5	125.1	116.5
Bu ₂ SnGlyGly·H ₂ O	121.7	6	1.37	2.65	5	115.5	110.7	124.6
Cy ₂ SnGlyGly	123.6	7	1.42	3.11	7	130.1	123.1	–
Cy ₂ SnGlyAla	122.9	7	1.41	3.09	7	129.5	122.6	–
Ph ₂ SnGlyGly	117.54	8	1.037	(–)2.235 ($\eta=0.805$) ^e	11	113.2	108.4	123.2

^aMe = methyl; Et = ethyl; Bu^u and Bu^t = butyl and tertiary butyl; Cy = cyclohexyl; Ph = phenyl; GlyMet = glycylmethioninate; GlyGly = glycylglycinate; AlaHis = alanylhistidine; MetMet = methionylmethioninate; TrpAla = tryptophanylalaninate; GlyTyr = glycyltyrosinate; GlyVal = glycylvalinate; GlyAla = glycylalaninate; see Figure 14.14 and caption for the general structure.

^bIsomer shift with respect to RT Ca¹¹⁹SnO₃.

^c ^{119}Sn nuclear quadrupole splitting.

^dMeasured on solid absorber samples at 77.3 K.

^e(I): Values extracted from the point-charge model rationalization of ΔE data by assuming a regular trigonal bipyramidal structure (Figure 14.14) except the C–Sn–C angle; (II): values extracted from the equation $\Delta E = 4\{R/[1 - (\frac{1}{2})\sin^2\theta]\}^2$. See text. (I), (II): data reported in Refs 1–11 or calculated in this work.

^fData from a Mössbauer–Zeeman spectrum; $\eta = \frac{(V_{\text{ax}} - V_{\text{xy}})}{V_{\text{z}}}$ is the asymmetry parameter. See text.

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Table 14.4 Correlation of C–Sn–C angles in five coordinated, trigonal bipyramidal $\text{Alk}_2\text{Sn}^{\text{IV}}$ -dipeptide complexes in solution phase, extracted from the hyperfine parameters ^{119}Sn Mössbauer nuclear quadrupole splitting, with values obtained from the coupling constants $|^2J(^{119}\text{Sn}, ^1\text{H})|$ and $|^2J(^{119}\text{Sn}, ^{13}\text{C})|$ measured by ^1H and ^{13}C NMR spectroscopy

Compound ^a	Solvent ^b	δ^c (mm s ⁻¹)	ΔE_{qp}^d (mm s ⁻¹)	$ ^2J(^{119}\text{Sn}, ^1\text{H}) $ (A); $ ^2J(^{119}\text{Sn}, ^{13}\text{C}) $ (B) (Hz)	Ref.	C–Sn–C angles (°) estimated from:	
						ΔE^e	$^2J, ^1J^f$
$\text{Me}_2\text{SnGlyGly}$	$\text{CH}_3\text{OH}; \text{CD}_3\text{OD}$	1.23	3.23	81.3 (A)	1	133.7	126.1
	$\text{H}_2\text{O}; \text{D}_2\text{O}$	1.24	3.27	82.2; 82.3 (A); 649.2 (B)	1, 2	134.9 ^g	127.1
$\text{Me}_2\text{SnGlyVal}$	$\text{CH}_3\text{OH}; \text{CD}_3\text{OD}$	1.21	3.09	78.0 (A)	2	129.5	122.6
	$\text{H}_2\text{O}; \text{D}_2\text{O}$	1.19	2.98	80.0; 82.0 (A)	2	126.2 ^g	119.8
$\text{Me}_2\text{SnGlyMet}$	$\text{CH}_3\text{OH}; \text{CD}_3\text{OD}$	1.22	3.13	82.0; 84.0 (A)	2	130.7	123.6
	$\text{H}_2\text{O}; \text{D}_2\text{O}$	1.19	2.99	80.0 (A)	2	126.5 ^g	120.0
$\text{Et}_2\text{SnGlyGly}$	$\text{CH}_3\text{OH}; \text{CD}_3\text{OD}$	1.33	3.49	632.84 (B)	3	141.7	132.8
							132.3

^aAbbreviations as in Table 14.3.

^bDeuterated solvents were employed for the solutions submitted to NMR.

^c ^{119}Sn isomer shift with respect to RT $\text{Ca}^{119}\text{SnO}_3$.

^d ^{119}Sn nuclear quadrupole splitting.

^eMeasured in solutions frozen to glassy phases by immersion of the sample holders into liquid N_2 ; data taken at 77.3 K.

^fData under (I) and (II): obtained as described in Table 14.3 [footnote d].

^gCalculated according to Ref. 170 by the equations ($\theta = \text{C–Sn–C bond angle}$): $\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$; $|^1J| = 11.40 - 875$.

^hReferred to supposedly undissociated species (see text).

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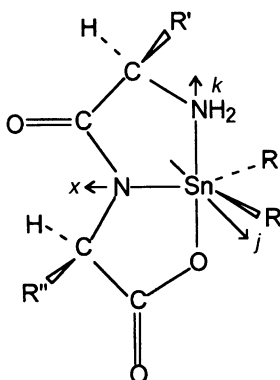


Figure 14.14 Idealized regular trigonal bipyramidal structure of diorganotin(IV)-dipeptide complexes. R = Alk, Ph; R', R'' are related to the dipeptides listed in Tables 14.3 and 14.4. x, j, k are the directions of the collective components of the diagonalized EFG tensor (equation 14.20).

From these calculated parameters, assuming regular trigonal bipyramidal structures and accounting for the condition $|\Delta E_{\text{exp}} - \Delta E_{\text{calcd}}| \leq \pm 0.41 \text{ mm s}^{-1}$ [102], the Alk_2Sn -dipeptide complexes are assigned to two different classes according to the coordinating situation of COO groups as reflected by the ΔE_{exp} data [168] (Table 14.3). Besides, the sign of ΔE and the value of η for $\text{Ph}_2\text{SnGlyGly}$, as extracted from Mössbauer-Zeeman spectroscopy (Table 14.3) correspond essentially to the calculated data. Lastly, structures in solution phases (Table 14.4) essentially coincide with those in the solid state (Figure 14.14), as far as $\Delta E_{\text{exp,calcd}}$ values are concerned.

The trends shown by ΔE_{exp} values (Tables 14.3 and 14.4) are better interpreted in terms of distortions from the ideal geometry in Figure 14.14, rather than in terms of the coordinating properties of axial COO. By this method, only the predominant contributions to the EFG due to the highly covalent Sn-C bonds, as shown by the $|p.q.s.|$ values, are accounted for, and the dependence of ΔE_{exp} from C-Sn-C angles is evaluated. From the data in Table 14.3, an acceptable agreement is detected with X-ray diffractometry data (see references in Table 14.3), as well as with values calculated by the MNDO approach [83]. In the solution phase, the agreement between C-Sn-C angles from ^{119}Sn ΔE_{exp} (in frozen solutions) and NMR coupling constants (by Lockhart's procedure [170]) appears to be excellent (Table 14.4). Lastly, a reasonable accordance is also observed between the solid state C-Sn-C angles from ^{119}Sn Mössbauer and solution phase data from NMR coupling constants (see references in Tables 14.3 and 14.4).

From the foregoing discussion, the reliability of structural assignments, even those concerned with fine details, extracted from ^{119}Sn Mössbauer parameters of organotin(IV) species, is clearly demonstrated. In particular, ^{119}Sn Mössbauer structural studies of aqueous solutions, as well as on solutions in

the medium employed for example pharmacological investigations [171], help in QSAR studies; in fact, in the case of $\text{Me}_2\text{SnGlyGly}$ species, such as that in Figure 14.14, axial ligand atoms substituted by solvent molecules are assumed to occur [166, 168, 171], according to additive model treatment [171]. This would imply that the dipeptide carries the $\text{Me}_2\text{Sn}^{\text{IV}}$ moiety, bound to the peptide nitrogen [171], into biological systems, where the organotin moiety develops its toxicological properties.

The correlation between experimental ^{119}Sn ΔE values and bond distances for $\text{Sn}-\text{Cl}$ and $\text{Sn}-\text{Br}$ in octahedral complexes SnCl_4L_2 , SnCl_5L^- and SnBr_4L_2 , as deduced from X-ray crystallography [172–174], should be mentioned here as a further example of the usefulness of Mössbauer spectroscopy for the estimation of structural parameters.

14.10.2 Interaction of organotin(IV) compounds with biological molecules and systems: structures and dynamics

Interest in this field arises from (1) the wide practical uses of organotins [132]; (2) the consequent dispersion into the environment [159, 162] and (3) their interaction with living organisms [175, 176], besides, (4) their pharmaceutical and medicinal applications [175, 176].

Studies on organotins bound to biological molecules, as well as on organotins in biological systems, by ^{119}Sn Mössbauer spectroscopy, make it possible to establish at least the type of bonding and coordination at Sn, irrespective of the molecular complexity of the ligand molecule, or of the nature of the whole system. In addition, the dynamics of tin nuclei may be investigated. The procedures discussed in sections 14.7 and 14.8 may be employed for these purposes. Here, examples are discussed concerning the interaction of organotin(IV) compounds with (1) rat and feline haemoglobins, (2) calf thymus DNA and (3) human erythrocytes, rat liver mitochondria, cells of the fungus *Ceratocystis ulmi* and their constituent units. A number of studies have been carried out in these fields, e.g. on the bonding of $\text{Et}_3\text{Sn}^{\text{IV}}$ to feline haemoglobin [177–182] and on the interaction of $\text{Bu}_2\text{Sn}^{\text{IV}}$ and $\text{Oct}_2\text{Sn}^{\text{IV}}$, as well Sn^{II} , with DNA [183–187].

The structural attributions extracted from the point-charge model rationalization of the Mössbauer parameters, nuclear quadrupole splittings and ΔE , are given in Table 14.5 and Figure 14.15.

The results of studies on the dynamics of ^{119}Sn nuclei in organotin(IV)–DNA (calf thymus) condensates [188] are reported in Table 14.6. The effective vibrating masses $M=\text{EVM}$ (eqns. 14.13 and 14.14) have been assumed to correspond to those of the molecular units $\text{Alk}_2\text{Sn}(\text{DNA monomer})_2$ and $\text{Alk}_3\text{Sn}(\text{DNA monomer})$ on the basis of estimates of N (the number of absorber resonant atoms per square centimeter; eqn 14.17) from the areas of the Mössbauer doublets [188]. Debye temperatures, ϑ_D , in Table 14.6 refer to these EVM data [188], essentially corresponding to the ϑ_D values

Table 14.5 The structure of the tin environment in organotin(IV)–hemoglobin^a, organotin(IV)–DNA native^a, and organotin(IV) in biological systems^a, from experimental and calculated ¹¹⁹Sn Mössbauer parameters

Interaction	$\Delta E_{\text{exp}}^{\text{b}}$ (mm s ^{−1})	Point-charge model calculations ^c			Ref.
		Structure ^d	$\Delta E_{\text{calcd}}^{\text{e}}$ (mm s ^{−1})	η^{f}	
<i>(A) Hemoglobin with:</i>					
Alk ₃ Sn ^{IV g}	1.53–1.94	(I)	−1.76	0.00	1, 2
Et ₃ Sn ^{IV}	−1.76 ^h ; η =0.00 ^h	(II)	−1.82 ⁱ	0.00	1, 2
Me ₂ Sn ^{IV}	2.10–2.30	(III)	(−)2.07	0.92	3
		(IV)	+2.22	0.11	3
Me ₂ Sn ^{IV} –(SR) ^j	2.19; 2.39	(V)	(±)2.03	1.00	3, 4
Me ₂ Sn ^{IV} –(SR) ₂ ^j	1.58–2.48	(VI)	(−)1.84	0.99	3, 4
<i>(B) DNA with:</i>					
Alk ₃ Sn ^{IV k}	3.77–3.89 ^l	(VII)	−3.87	0.00	5, 6
Et ₃ Sn ^{IV}	−3.68 ^h ; η =0.12 ^h	(VII)	−3.87	0.00	5, 6
Alk ₂ Sn ^{IV k}	4.35–4.49 ^l	(VIII); (IX)	+4.60	0.00; 0.03	5, 6, 7
Et ₂ Sn ^{IV}	+ 3.77 ^h ; η =0.00 ^h	(VIII); (IX)	+4.60	0.00; 0.03	5, 6, 7
Me ₂ Sn ^{IV}	3.52 ^m	(X)	3.52 ⁿ	–	6
Et ₂ Sn ^{IV}	3.56 ^m	(X)	3.55 ⁿ	–	6
Point-charge model calculations ^c					
			C–Sn–C angles (°)		
			[Struct. (X), (XI)]		
			and C–Sn–A angles		
			[Struct. (XII), (XIII)]		
<i>(C) Interaction of biological systems^a with:</i>	$\Delta E_{\text{exp}}^{\text{b}}$ (mm s ^{−1})	Structure ^d			Ref.
Alk ₂ Sn ^{IV o, p}	2.75–3.33	(XI)	113–129		8
Me ₂ Sn ^{IV p}	3.77	(X)	152		8
Alk ₃ Sn ^{IV g, p, q}	2.96–3.48	(XII)	102–90		8, 9
Et ₃ Sn ^{IV q}	1.67; 2.78	(XIII)	116; 109		9, 10
Ph ₂ Sn ^{IV p}	2.47–2.96	(XI)	116–131		8
Ph ₃ Sn ^{IV p, r}	2.75–3.13	(XII)	98–90		8, 11

^aAssumed as (Alk₃Sn)₂- and (Me₂Sn)₂-hemoglobin tetramer (rat and cat); Alk₃Sn(DNA monomer) and Alk₂Sn(DNA monomer)₂, calf thymus DNA. Biological systems: (1) human whole erythrocytes, erythrocyte membranes, ghost cells, and the cytoplasm; (2) rat liver mitochondria, and the mitochondrial membrane; (3) cells of the fungus *Ceratomyces ulmi*, and cell walls. See text.

^bNuclear quadrupole splitting. Determined on solid absorbers at 77.3 K, unless otherwise stated.

^cSee sections 14.7.2 and 14.10.1. Literature data are reported here together with additional values estimated in the present context.

^dFigure 14.15.

^eSign in parentheses means uncertainty in the assignment for $\eta \approx 1.00$. Values for (I) and (II): new estimates.

^fThe asymmetry parameter ($|V_{xx} - V_{yy}|/V_{zz}$).

^gAlk = Me, Et, Buⁿ.

^hFrom Mössbauer–Zeeman spectroscopy.

ⁱC–Sn–S angles = 100°.

^jSR are thiol groups of 2-mercaptoethane sulfonate, L-cysteinate and L-penicillamine.

^kAlk = Me, Et.

^lData for gelled condensates at 77.3 K, and for lyophilized absorber samples measured in the temperature ranges: Alk₃ = Me₃, $T = 77.3$ –220 K; Alk₃ = Et₃, $T = 15$ –221 K; Alk₂ = Me₂, $T = 77.3$ –293 K; Alk₂ = Et₂, $T = 15$ –288 K. For Alk₂Sn^{IV}, ΔE_{exp} data refer to the larger doublet in the fittings of experimental spectra with two doublets.

^mInner doublet of lyophilized samples as in footnote l.

ⁿC–Sn–C angle = 143°; 144°. Calculated by the procedure for distorted structures, equation 14.12.

^oAlk = Me, Buⁿ.

^pBiological system 1, footnote a.

^qSystem 2, footnote a.

^rSystem 3, footnote a.

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for the model polymeric complexes $\text{R}_2\text{Sn}(\text{adenosine monophosphate}) \cdot 2\text{H}_2\text{O}$ ($\text{R} = \text{Me, Bu}^n$; $\vartheta_{\text{D}} = 65.0$ and 52.0 K) [188] and $\text{R}_2\text{Sn}[\text{O}_2\text{P}(\text{OPh})_2]$ ($\text{R} = \text{Me, Et, Bu}^n$, $\vartheta_{\text{D}} = 56.2, 57.1$ and 42.3 K) [188], where EVM is taken as the molecular weight.

On the basis of the fingerprint criteria reported in section 14.8, based upon (1) slopes $d \ln A/dT$, and (2) $\langle x^2 \rangle(T)$, the following may be assumed (from Table 14.6):

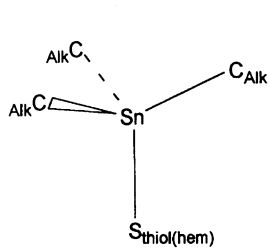
- $\text{Alk}_2\text{Sn}(\text{DNA monomer})_2$: (1) polymeric; (2) bi- and tridimensional, polymeric;
- $\text{Alk}_3\text{Sn}(\text{DNA monomer})$: (1) monomer–polymer border zone; (2) monomeric, or monodimensional polymeric.

It is worth mentioning here that the order of magnitude of the ‘relative’ $\langle x^2 \rangle$ data in Table 14.6 (which, on the other hand, essentially agree with the ‘absolute’ values) [188], correspond to data $\langle x^2 \rangle$ concerning the dynamics of Fe in deoxymyoglobin and metmyoglobin [188], as well as to the internal motions of proteins and nucleic acids [189].

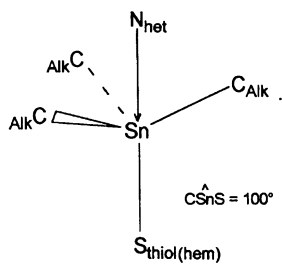
Lastly, structural assignments by the correlation of the ^{119}Sn Mössbauer isomer shift parameter, δ , with the partial atomic charge on tin, Q_{Sn} , as described in section 14.7.1, have been effected for a series of assumed five-coordinated species $\text{Alk}_2\text{Sn}^{\text{IV}}$ - and $\text{Alk}_3\text{Sn}^{\text{IV}}$ -hemoglobin and -DNA, as well as for series of model systems in the solid state and in solution phases [90, 190].

The structures thus inferred for the hemoglobin and DNA complexes correspond to those extracted from ΔE rationalizations (Table 14.5 and Figure 14.15).

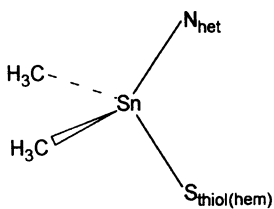
It is concluded that the octahedral $\text{Alk}_3\text{Sn}^{\text{IV}}$ site, (IX) in Figure 14.15, could originate from the interstrand linking of the DNA double helix in the toroidal DNA condensates, which would cause the ‘polymeric’ character of



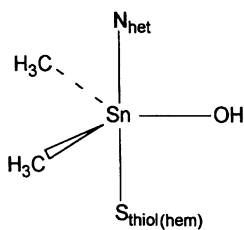
(I)



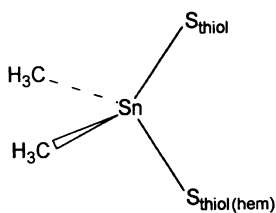
(II)



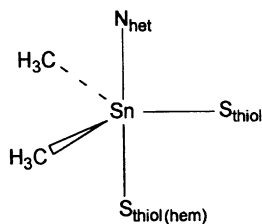
(III)



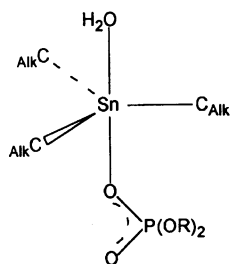
(IV)



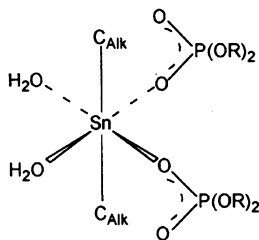
(V)



(VI)



(VII)



(VIII)

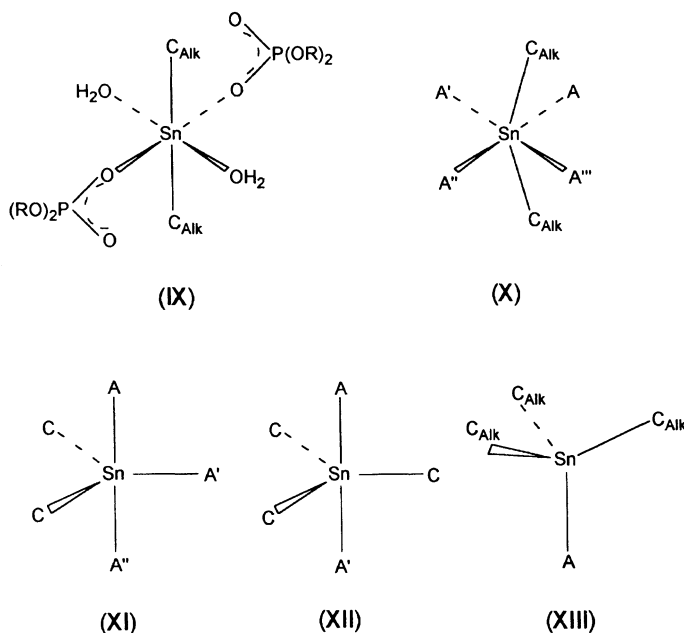


Figure 14.15 The structure of tin environments in: (I)–(VI): [trialkyltin(IV)]₂ and [dimethyltin(IV)]₂–rat hemoglobin tetramer, and [triethyltin(IV)]₂–[cat hemoglobin tetramer]. $S_{\text{thiol(hem)}}$ and N_{het} are thiol sulfur and heterocyclic nitrogen atoms from cysteine 13 and histidine 113 of the hemoglobins; S_{thiol} are donor atoms from further thiolated ligands. Regular structures are assumed except for (II). (VII)–(X): trialkyltin(IV)(DNA monomer) and dialkyltin(IV)(DNA monomer)₂, from DNA calf thymus. Regular structures, except (X). (X)–(XIII): diorganotin(IV) and triorganotin(IV) in biological systems, distorted structures: See Table 14.5 and text.

Table 14.6 The dynamics of tin nuclei in organotin(IV)–DNA (calf thymus) condensates^a

Organotin(IV)–DNA monomer unit ^b	$-10^3 \text{ d} \ln(A_T/A_{77.3})/\text{d}T$ (K ⁻¹) ^c	$10^2 \langle x^2 \rangle (\text{\AA}^2)^{\text{d}}$ at 77.3 K	200 K	$\vartheta_D(\text{K})^e$
$\text{Me}_2\text{Sn}(\text{DNA monomer})_2$	1.220 (0.996)	0.646	1.672	47.3
$\text{Me}_3\text{Sn}(\text{DNA monomer})$	1.555 (0.989)	0.823	2.130	53.5
$\text{Et}_2\text{Sn}(\text{DNA monomer})_2$	1.250 (0.996)	0.662	1.713	45.9
$\text{Et}_3\text{Sn}(\text{DNA monomer})$	2.045 (0.993)	1.083	2.802	44.7

^aDetermined by variable temperature ^{119}Sn Mössbauer spectroscopy, section 14.8. Data from Ref. 188.

^bFreeze-dried condensates employed as absorber samples.

^cSlopes of functions: total area under the resonant peaks vs. temperature; correlation coefficients in parentheses.

^dThe mean square displacement of ^{119}Sn nuclei, calculated by equation 14.15, from aggregated f_a^{rel} data.

^eDebye temperature, obtained from equation 14.14.

tin environments [188]; the trigonal bipyramidal $\text{Alk}_3\text{Sn}^{\text{IV}}$ unit, (VII) in Figure 14.15, would be instead appended to the DNA double helix, thus showing a 'monomer'-like dynamic behavior [188]. These assumptions are in line with the data concerning organotins embedded into synthetic monomeric as well as polymeric materials, whose dynamics appear to be independent of the degree of polymerization of the substrate (section 14.9.1).

14.10.3 Solution chemistry

Structure and bonding in solution may be investigated by Mössbauer spectroscopy of glassy phases, obtained by rapidly freezing the solution by immersion of the absorber sample into, for example, liquid N_2 . Studies in the field have been amply reviewed, including the estimation of equilibrium constants by measurements of areas under the resonant Mössbauer lines [11, 191].

Recent investigations on tin derivatives have been concerned with the determination of species present in solution phases which had reacted with biological molecules, such as hemoglobins and nucleic acids, in order to understand better the coordination reactions as well as the nature of the products [106, 192–195]. Thus the bonding to tin atoms by buffer constituents [192] and complex formation and stoichiometry by functions of ΔE vs. [ligand] [106, 193] have been investigated. Besides, in the context of studies on the antitumor activity of organotin(IV) derivatives [196, 197], the composition of species in the vehicle of administration (e.g. in mice) has been investigated by this technique, in order to obtain detailed information on the relationship between structure and antitumor activity [171, 198–201].

Representative examples are reported here, concerning $\text{Me}_2\text{Sn}^{\text{IV}}$ species. In ethanol solution the *trans*- Me_2 octahedral complex $\text{Me}_2\text{SnCl}_2(\text{C}_2\text{H}_5\text{OH})_2$ is formed [194, 195] (Figure 14.16); in aqueous solution, the gradual hydrolysis of the $\text{Me}_2\text{Sn}^{\text{IV}}$ moiety is reflected by the functions \bar{n} , ΔE vs. pH (Figure 14.17), in going from the octahedral aquated species $\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4^{2+}$ to tetrahedral $\text{Me}_2\text{Sn}(\text{OH})_2$ [202]. The latter, present at neutral and basic pH, reacts

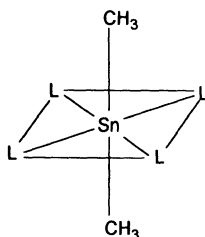


Figure 14.16 $\text{Me}_2\text{SnCl}_2(\text{C}_2\text{H}_5\text{OH})_2$, $\Delta E_{\text{exp}} = 4.05$ (in frozen ethanol solution); $\Delta E_{\text{calcd}} = +4.12$. (See Refs 194 and 195). Calculation is effected by considering the EFG tensor to be produced only by the Sn–C bond electrons (section 14.7.2).

with aqueous phosphate and D-ribose-5-phosphate, yielding mainly 1:1 and 1:2 complexes where the $\text{Me}_2\text{Sn}^{\text{IV}}$ moiety would be embedded into trigonal bipyramidal or octahedral (presumably distorted) species [203] (Figure 14.18).

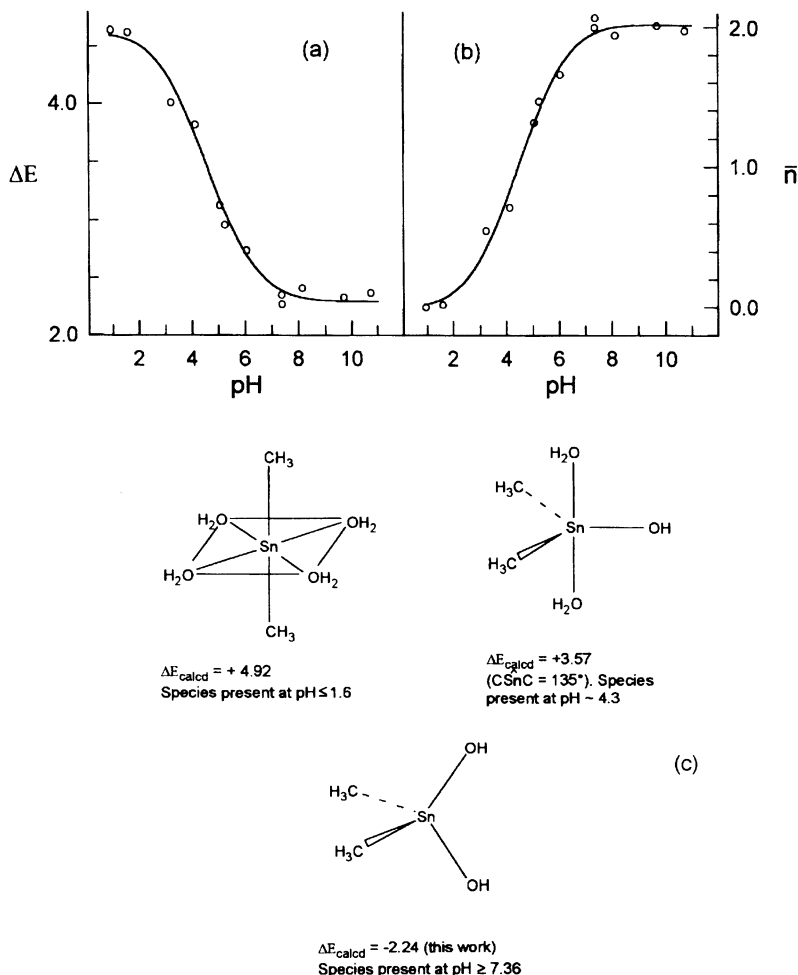


Figure 14.17 (a) ^{119}Sn Mössbauer nuclear quadrupole splitting, ΔE (mm s⁻¹) as a function of pH in aqueous (frozen) solutions [202]. (b) Function \bar{n}/pH , where \bar{n} , the average number of OH^- coordinated to Sn in $\text{Me}_2\text{Sn}^{\text{IV}}$, is extracted by [204]:

$$p = p_0 + \bar{n} \frac{(p_N - p_0)}{N} \quad (14.21)$$

where p are values of ΔE at a given \bar{n} ; p_0 and p_N are ΔE values inherent to the cation $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ and to the saturated species $\text{Me}_2\text{Sn}(\text{OH})_2$ ($N=2$), respectively [202, 204]. (c) These structures are assigned to representative species [202] by the application of the point-charge model procedures (section 14.7.2).

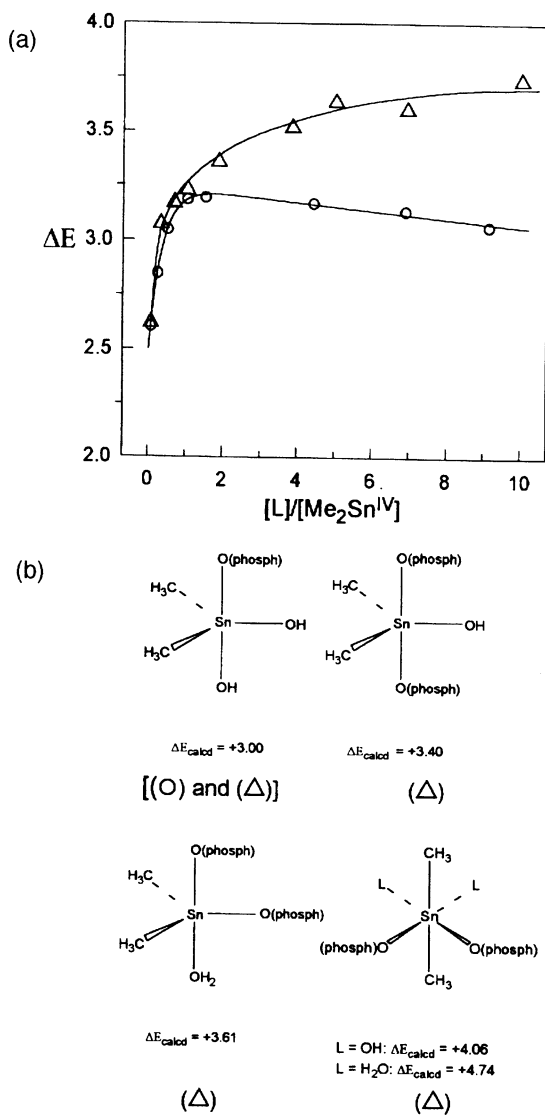


Figure 14.18 (a) The ^{119}Sn Mössbauer 'titration' of $(\text{CH}_3)_2\text{Sn}(\text{OH})_2$ with $\text{L} = \text{H}_n\text{PO}_4^{(3-n)-}$ (Δ) and D-ribose-5-phosphate (O). (Adapted from Ref. 204). (b) Possible complex species, formed in the solutions, according to point-charge model calculations of ΔE [203].

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15 The analysis of organotin compounds from the natural environment

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15.1 Introduction

Tin is a group 14 metal which is found naturally as cassiterite [tin(IV) oxide]. Common uses are as an alloy (i.e. in pewter, solder and bronze) and in the electroplating of steel [1–3]. Early records indicate that tin has been in use for 5000 years, its use in an alloy with copper to form bronze was the basis of early civilization in the Western world. Compounds of tin have been used in dye preparations from Egyptian times; the first recorded organometallic compound of tin was diethyltin diiodide, which dates from 1849.

Metallurgical uses account for up to 90% of the world production of tin; compounds of tin are now of increasing importance to the tin industry. The inorganic compounds of tin are now used for a number of applications, e.g. tin(II) chloride and sulphate are used in the electroplating of steel, tin(IV) oxide is used extensively in the ceramic industry as a pigment and tin(IV) chloride is used to deposit films of tin(IV) oxide on glass. The organometallic compounds of tin are used as marine biocides for antifouling paint, wood preservatives and heat/light stabilizers in the PVC industry [4, 5].

The properties of organotins (R_nSnX_{4-n}) are determined by the number of alkyl groups (R) present; the properties rely less on the nature of the X group, but it does have some effect. The versatile properties of this group of chemicals have led to considerable growth in their use between 1960 and 1985; in 1975 their use was approximately 5000 tonnes per annum, while in 1985 it was thought to exceed 40 000 tonnes [6]. The most common organometallics are of the form $R_{4-n}SnX_n$ ($n=0-4$). Table 15.1 gives an overview of the alkyl substituents and their effect on usage. The plastics industry accounts for two-thirds of the total consumption of organotin compounds as PVC stabilizers [3].

15.1.1 Toxicity

The toxicity of organotin compounds is almost as wide ranging as their properties [2–4, 7]. The inorganic tin compounds and the element itself are relatively non-toxic. This low toxicity is attributed to slow absorption in the gut (mammals), inhibiting any direct effect on the cellular make-up. However, the organotins exhibit a far more complex behaviour: they are absorbed into soft tissue much more easily, and for triphenyltins up to 10% of the total ingested compound is absorbed in bovine species. The toxicity is, however,

Table 15.1 Uses of various organotin species [3]

Compound	Application
R_nSn	
R = phenyl, octyl, butyl	Starting materials for other organotins
R = butyl	Catalysts
R = phenyl	Oil stabilizers
R_2SnX	
R = butyl	Biocides, e.g. antifouling paints, wood preservatives, paint preservatives
R = phenyl	Agricultural fungicides, antifouling paints
R = cyclohexyl, neophyl	Miticides
R_2SnX_2	
R = methyl, butyl, acetate ester	PVC heat stabilizers, catalysts, polyurethane formation
$RSnX_3$	
R = methyl, butyl, octyl, acetate ester	PVC heat stabilizers

species specific, the only organotin compounds which exhibit toxic behaviour to humans being the short-chain methyl and ethyl derivatives; the longer aliphatic chains tend to exhibit little mammalian toxicity. Some ring systems can also be considered harmful to mammalian life.

The toxicity of organotin compounds is related to the number of alkyl groups present in the $R_{4-n}SnX_n$ formula. The tetraorganotins can be considered toxic in the long term as the decomposition of these compounds results in the formation of the trialkyl form. Studies have shown this process to occur particularly well in the liver. The trialkyltins are the most toxic form of organotin, but the nature of the alkyl group determines the specificity towards a particular species. Table 15.2 below gives a brief outline of trialkyltin toxicity [4].

The toxicity of the mono- and diorganotin species is not extensively documented in the same way as for the triorganotins, but information on their action exists. The diorganotins are more toxic than the mono-organotin compounds, which are considered to be non-toxic. The level and specificity of diorganotin toxicity is determined by the chain length of the aliphatic derivatives, and by the nature of any ring system present.

The mode of action of both tri- and dialkyltins is well documented. The bioactivity is thought to stem from protein binding, possibly at cysteine and

Table 15.2 Species specificity of triorganotin compounds

Species	Most active R in R_3SnX
Insects	CH_3
Mammals	C_2H_5
Gram negative bacteria	$n-C_3H_7$
Gram positive bacteria, fish, fungi, molluscs, plants	$n-C_4H_9$
Fish, fungi, molluscs	C_6H_5
Fish, mites	cyclo- C_6H_{11}
	$C_6H_5(CH_3)_2CCH_2$

histidine sites. This can have an effect on membrane function, causing disruption to ion transport and signal transduction. They have also been found to cause atrophy of the thymus gland, but it is thought that the effects of exposure are in general reversible; cell recovery has been noticed as little as 24 h after peak damage had occurred. There has also been evidence that the organotins exhibit neurotoxicity, particularly trimethyltin (damage to the CNS) and triethyltin (brain/spinal cord oedema).

There has been one large scale human poisoning due to contamination of a formulation used to cure boils in France in 1954. The oral preparation Stalinon, primarily linoleic acid, was administered orally. The contaminant was a mixture of tri-, di- and monoethyltin, and the death toll was 102, with 200 others suffering non-fatal effects of exposure. A smaller scale industrial poisoning involving trimethyltin also led to one death and two seriously disabled.

15.1.2 Applications of organotin compounds

There are three main uses of organotins which have significance to environmental pollution, namely antifouling paints, wood preservatives and agricultural preparations. There are several other uses of these compounds, but these are not as significant from an environmental point of view.

The use of organotins in agriculture originated in the early 1960s, the compounds triphenyltin acetate (Brestan) and the corresponding hydroxide (Du-Ter) being marketed by Hoechst and Phillips Duphar, respectively [8]. These compounds were used to combat potato blight, the disease which had caused widespread famine in 19th century Ireland. The existing treatment, which was based on a copper agent, required 10 times the dose for a similar effect. These compounds have also been used for the control of leaf spot (sugar beet and celery), blast (rice), berry disease (coffee) and for algal growth (paddy rice) [8, 9].

More complex systems are used as pesticides to control mites, e.g. the compound tricyclohexyltin hydroxide (Piltran) is very effective against many mite species, i.e. red spider mite, Pacific spider mite and citrus rust mite among others [8]. This compound and other similar formulations have many advantages, including a high specificity for target organisms and little toxic effect on natural predators (i.e. predatory mites and honey bees). It also has an antifeeding effect on other insects (i.e. caterpillars) and therefore its mode of action is prophylactic, as opposed to systemic. This final point is important in preventing contamination of the food chain.

The use of organotin compounds as a wood preservative relies on similar properties to the agricultural applications. The fungicidal action of the organotins is used to protect wood, which is still an important building material in many parts of the world. Bis(tributyltin) oxide has been used for this application since 1958 [2, 5]. They are only poorly soluble in water and hence

require the use of organic solvents for application, usually a 1–3% solution in petroleum ether. This presents a problem of solvent disposal which induces additional expense. There are also considerations of health and pollution, both in the environment and in the workplace.

Some of these problems have been overcome by the use of a quaternary ammonium salt in combination with TBT oxide as an aqueous suspension. There are also specially developed preparations which are water soluble, while retaining the fungicidal properties [2].

From an environmental point of view, the use of organotins as marine biocides in antifouling paints is probably the most significant [10–13]. There are two main advantages to using antifouling paints. In the case of wooden vessels the advantages are obvious, the degradation of timber components in seaborne vessels having obvious consequences. Wood rot as well as parasitic infections slowly weaken the timber and reduce the seaworthiness of the vessel. In the case of vessels with metal or composite hulls the advantage comes from the reduced drag and improved fuel efficiency achieved by elimination of mollusc adhesion to the hull.

The sea is the vital intercontinental link in most of the largest import/export industries. Oil, motor vehicles and large scale machinery are transported almost exclusively along the shipping lanes of the world. The build-up of barnacles, sea grass and the huge amount of diverse species which attach to hulls of seagoing vessels significantly increases the drag of the underside of the vessel. Increased drag causes lower fuel efficiency and consequently higher prices. The use of marine biocides, which are bound in paint formulations and undergo slow release, significantly slows down this build-up. These paints work by creating a biocidal barrier between the ship and the surrounding water.

The main organotin biocide is TBT, which is used in a number of different formulations [1, 2, 4, 5]. This compound replaced cuprous oxide, which was used prior to the 1960s. The main advantage of TBT is that the more powerful biocidal activity means that lower concentrations can be used in the formulations. The amount of tributyltin present is usually 10–15% w/w, which is sufficient for 1–2 years of protection after which the hull must be repainted. There are several ways of incorporating the organotin moiety into the paint formulation, the most common way now being to chemically bind the TBT as a side chain on a methylacrylate polymer; the exposed TBT groups are hydrolysed in the water. This process releases the TBT species to the local environment, as the paint becomes eroded, leading to the regular exposure of a fresh TBT-containing surface. However, in time the surface becomes swollen with water and repainting is required.

The main alternative is to use a rubber-based coating, which can hold larger amounts of TBT. The higher concentrations are due to the mode of release, which in this case is a diffusion/dissolution process. When the TBT is incorporated into the paint it affects the properties of the paint, which

limits the loading to a maximum of 30% w/w. The rubber formulations can accommodate up to 50% w/w, and release of TBT is controlled by a physical process (diffusion), not chemical (hydrolysis) as with the copolymer paints. This has been claimed to extend the lifetime of the protection to 7 years. The problem with the rubber coating is the difficulty in application; paints are simple to apply but rubber coatings present a more complex problem and tend to be restricted to small applications such as sonar buoys and other small devices.

15.1.3 Environmental release of tin compounds

Since the Industrial Revolution man has caused a redistribution of elements, and through mining and other heavy industry the natural balance of the elements has been disrupted. In terms of pollution this is usually referred to as anthropogenic input. There is also of course a natural redistribution of the elements caused by weathering, erosion and natural disasters.

Tin is unusual for two reasons. First it is a historic element and has been used for 5000 years; second unlike similar heavy metals it is not considered to be toxic, and has even been postulated as an essential element. Tin itself is not often found in high concentrations in the environment, except in close contact to industrial emission points and mining activity. There is also little evidence of significant inorganic tin compounds in the environment, with the exception of industrial effluent run-offs.

The question of organotin compounds in the environment is a complex problem which is best divided into three areas; anthropogenic input, biocidal/pesticidal input and bioalkylation. Anthropogenic input refers to the release of organotin compounds during production, use and disposal. This type of release is common to some extent for all industrial chemicals. It also is normally regulated by local law, and should be controlled to within non-harmful levels. This sort of pollution is usually localized to production facilities, storage areas and waste disposal areas which are simple to monitor, ensuring a reduction in the risk to both human life and the environment.

The main concern in the area of environmental organotin contamination is the use in biocides and pesticides [10–13]. In both of these applications, release into the local environment is essential for them to be effective. Pesticides are sprayed on crops and storage areas to control damage, while whole biocides are released from the antifouling paints in an effort to lower the build-up of marine organisms. In both applications the aim is to create a prophylactic barrier to the target organism without having a detrimental effect on the subject or its local environment.

In order to ensure the best possible protection, excess quantities of both pesticides and biocides are used, although this excess will contaminate the local environment. In the case of pesticides the run-off from fields may

become polluted by organotins. This may be carried into the local rivers and lakes and affect the ecosystem in these areas. The problems of pollution due to agricultural chemicals are well documented. Antifouling paints are released in a different manner. After the ship has been repainted, short term release of biocide is very high due to the excess quantities on the surface. This release is reduced as the hull wears and the release becomes a diffusion process which is more controlled.

The use of organotin-based antifouling paints began to cause concern in the late 1970s, and was attributed as a possible cause of the declining oyster population along the Atlantic coast of the UK and France [10]. The effects of organotin compounds, in particular TBT, are now well documented and have recently been reviewed [10]. Detrimental effects have been noted at concentrations as low as 2 ng l^{-1} for oysters. The financial implication of TBT pollution on the oyster population was estimated to be \$150 million between 1977 and 1983 in Arcachon Bay, France [10]. This pollution is due to high traffic density in the area, particularly small pleasure craft. This has led to legislation banning the use of TBT on small boats (<25m length) in France and the UK. Legislation also exists restricting the use of TBT in the USA, Canada, New Zealand and Europe.

It should be noted that the use of TBT is still prevalent on large-hulled vessels, so there are still significant releases in large shipping ports and oil terminals as well as the open sea. It is difficult to quantify the open sea problem due to dilution factors but it could be a significant problem in the future as the overall load increases. The contamination of shellfish breeding grounds close to large terminals is also a significant problem. The detrimental effect on local ecosystems and the financial costs to the shellfish industry mean that constant monitoring of the problem is essential. This has led to the development of a large variety of sensitive and specific analytical methods for the extraction and analysis of environmental organotin compounds [7, 14, 15].

Biomethylation is the formation of organotin compounds in the environment through the action of microorganisms [2]. This is a well established phenomenon for a number of heavy metal elements in which the organism essentially converts an inorganic compound into a methyl derivative, using an enzyme. These processes cause a formation and/or redistribution of the organometallic species present in the environment. This makes organotin compounds among the most complex to analyse as there is possibly a mixture of many different compounds in any one sample. The process of biomethylation is therefore important in the case of both inorganic and organic tin pollution. These cannot be treated separately as the inorganic tin pollution could have undergone bioalkylation to an organic form.

This again emphasizes the need for methods which differentiate between a number of species, and also an efficient method for extracting the target compounds from the environmental matrix. In addition to bioalkylation, the

transfer of organic groups from one metal to another may occur. This is important when we consider the pollution caused by organolead compounds from petroleum products. There are large amounts of methyl- and ethyllead species in the environment, which could cause transmethylation under favourable conditions giving methylated tin derivatives and mixed organometallics.

The combination of factors in the environment gives the analyst an intriguing task with regard to organotin measurements. There are the two main polluting chemicals, TBT and TPhT, together with their degradation products (i.e. mono- and diorganotins) and methyl compounds which may form in the environment. Organotins may therefore be subject to both transmethylation and biomethylation giving mixed methyl, butyl and phenyl derivatives. This means that sensitivity, extraction and separation are particularly important.

15.2 Analysis of inorganic tin compounds

This section is intended to give an overview of analytical methods for total (inorganic) tin in environmental samples. Tin at low levels has been extensively determined spectrophotometrically with the use of various reagents. However, poor selectivity, complex sample processing and a lack of sensitivity preclude many of these techniques from application to environmental analysis [6].

Advances in modern instrumentation have allowed analysts to reduce complex sample preparation and increase both sensitivity and selectivity. Atomic absorption spectrometry (AAS) solves the problem of selectivity. However, there are interference and sensitivity problems for flame-based techniques, which means that some form of preconcentration must be applied. Hydride generation techniques, with AAS, atomic emission spectrometry (AES) and atomic fluorescence, have been used successfully for environmental samples giving appropriate sensitivity for these applications (detection limit $0.05\text{--}25\ \mu\text{g l}^{-1}$). Other forms of sample introduction have been used, such as a graphite furnace with AAS and inductively coupled plasma (ICP) with both AES and mass spectrometry (MS) [6]. Other less common techniques are neutron activation analysis and polarography. A recent review citing over 1000 references for elemental analysis has been published [16].

The sample processing for most of these instrumental techniques involves simple acid digestion followed by the determination; water samples may be introduced directly if appropriate preconcentration techniques are available. However, the usefulness of total tin determination is questionable. It is a relevant measure but techniques which identify the species are of far more use, particularly considering the toxicity of organotin compounds in relation to inorganic tin.

15.3 Analysis of organotin compounds

Early methods for the analysis of organotin compounds in the environment were also based around photometric techniques. Determinations at ppm levels have been achieved with a variety of colorimetric reagents, i.e. dithi-zone and Catechol Violet [6]. This can be improved to the ppb level with polarography and fluorimetric techniques. Again, these methods are all subject to extensive sample preparation which is best avoided for environmental samples. Often the extractions for these determinations are restricted to particular compounds, which is hardly adequate considering the wide range of compounds which are present in environmental samples.

The need to develop a sensitive method for the speciation of all the organometallic compounds in the environment has produced a large amount of literature and a number of techniques. These tend to be hyphenated techniques, i.e. the combination of a detection method, separation method and possibly a derivatization step [17]. These techniques can be divided into two classes, direct and indirect. Indirect methods involve a derivatization step prior to separation, which usually involves the formation of volatile tin compounds which are then separated and detected. Direct methods generally involve liquid chromatography techniques on the sample itself without any derivatization, although the sample may need some prior clean-up and/or extraction. Each technique has its advantages, direct techniques involving less processing and there is less opportunity for error by eliminating the derivatization step. However, for biota an extraction is necessary in order to use a direct technique, but some indirect methods have overcome this step by using an *in situ* derivatization. The indirect techniques often have improved sensitivity due to the elimination of background effects within the detector. However, background interference and matrix effects can be a problem with direct methods.

15.3.1 Extraction techniques

A short discussion of extraction techniques is appropriate as they are essential to a number of techniques. A recent review of extraction techniques is not directly aimed at organotin species but provides good coverage of a number of techniques [18]. The choice of extraction technique is usually defined by the matrix of the sample and the type of analysis. In general water samples do not need extraction for modern LC or derivatization techniques, but it is essential for Grignard techniques which require a non-aqueous solvent. For solid samples there are a number of different methods; for example, solvents, acids, enzymic and supercritical fluids are all used as the extraction liquor.

15.3.2 Direct techniques

The use of liquid chromatography for the speciation of organotin species was

first published almost 20 years ago. Since then there has been great interest in organotins in general as well as the use of HPLC to analyse environmental samples. HPLC has been restricted in its use by the complex problem of detector interface, which has reduced the number of detectors available and hence its use in diverse fields such as organometallics. However, increased research has provided solutions to this problem and hence the technique has become more commonplace.

The use of HPLC analysis for organotin compounds has recently been reviewed [15]. This section will provide an overview of the techniques and cover some more recent material. The common modes of separation for HPLC are reversed phase, normal phase and ion exchange, as well as some more esoteric techniques such as size exclusion. Detectors for HPLC are usually UV, fluorescence, refractive index or electrochemical. Reliance on these few detectors has brought many advances in the area of UV detection, the introduction of diode array spectrometers and similar research in electrochemistry.

In the analysis of organotin compounds the above detection systems are not ideal; the standard UV detector (254 nm) will only detect the phenyltins, but it has been used for this application in the earliest reported HPLC technique [19]. However, other organotin species do not contain appropriate UV chromophores, but some analysis has been done on the organotin polymers used in antifouling paints which are more suited to this technique [20, 21]. Generally more sensitive than UV, molecular fluorescence-based detectors require derivatization of the organotin species with a suitable fluorescing agent. This has been utilized in a number of techniques with the reagent morin [15] and more recently fisetin [22]. However, this introduces the uncertainty of an indirect technique by adding a reaction step. Electrochemical detectors in general lack the sensitivity required for environmental analysis, hence the literature is sparse [23]. Refractive index detectors are based on a general bulk property and are not very sensitive, but their use has been reported in the literature. However, they show inadequate detection limits in the region of 80–100 μg as Sn [20, 21, 24].

A common property of all the above mentioned detectors is their lack of selectivity, which is the basis of most metal speciation studies. The analysis of environmental samples is simplified by the use of metal-specific detection systems such as AAS, AES and atomic fluorescence [17]. This reduces problems caused by co-eluting peaks in chromatography and detector saturation from matrix components. However, these systems are not easily interfaced to liquid chromatography because they are not designed for the large volumes of mobile phase involved in liquid chromatography.

For atomic absorption spectroscopy the atomization of the sample is of prime importance as this is directly related to sample delivery and hence the interface to the HPLC. Flame atomic absorption has the ability to handle the volume but is not sensitive enough for environmental levels [15]. Electrothermal atomization overcomes the interferences caused by the flame

technique but relies on discrete sample introduction and is therefore unsuitable for on-line analysis. The problems caused by this have been overcome with the use of a fraction collector/autosampler arrangement. The use of this technique is further complicated by reactions of the analytes with graphite furnaces forming tin carbides. This is overcome by using a chemical modifier such as palladium [25].

The alternative method of sample introduction is the use of hydride generation as a post column derivatization. This in conjunction with a gas/liquid separator can be used for quartz furnace AAS and AFS. However, this is really an indirect technique and will be dealt with in that section.

The use of flame AES as an HPLC detector for organotins in the environment has not been reported, probably due to lack of sensitivity [15]. The use of a plasma as an emission source has now become more common. This increases the sensitivity as a consequence of a greater atomization efficiency. Of the two common types of plasma, ICP and MIP, only ICP is used with HPLC as MIP cannot handle nebulized introduction. The use of ICP-AES for organotin analysis has been reviewed [17, 26, 27].

Probably the most important application of plasma technology to organotin analysis has been through the use of HPLC-ICP-MS. The use of MS as a detector for ICP gives an increase in sensitivity over the AES technique which can amount to two orders of magnitude. This can lower absolute detection limits for organotin species to sub-picogram levels [15]. The low detection limits coupled with decreasing equipment costs have contributed to the success of this technique over recent years, and it is now the most successful HPLC-based technique for organotin analysis.

The drawbacks of this technique are related to the interface, nebulization and choice of mobile phase. The design of the interface is very important as problems at this stage in the analysis lead to peak broadening and poor resolution. As the flow rate from HPLC and the required rate for ICP are compatible (i.e. $0.2\text{--}1\text{ ml min}^{-1}$) there is no need for sampling or flow reduction here. The choice of nebulizer is important for all ICP analysis as matrix effects or high buffer concentrations can cause deposits and hence blockages. Basic concentric nebulizers have always suffered from this problem. This has been overcome by redesigning the nebulizer head, and the newer nebulizers use a 'V groove' to run the sample into a gas stream. This produces a finer spray, improving the efficiency as less is lost in the spray chamber. Direct injection nebulizers have also been used to great effect in organotin analysis [28].

The other important part of the interface is the spray chamber. Rivas *et al.* tested three chambers as part of a measurement and testing programme for organotin speciation [29]. The high-volume double pass chamber (Scott-type) showed good resolution of peaks and the best signal to noise ratio when compared to a single pass chamber and a mini double pass chamber.

Until recently the direct interfacing of HPLC to MS has received little

attention, again probably due to interface problems. The techniques available for sample introduction are thermospray and ion spray. Both are covered in a recent review of organotin LC-MS analysis [30], and receive attention in a review of foodstuff analysis [31]. These techniques are, however, very specialized and subject to a number of difficulties. Recent papers by Lawson and coworkers cover the ion spray (cf. electrospray) technique and a particular thermospray interface [32, 33]. Both techniques of analysis are successful, but it is recognized that they are yet to become standard methods of analysis.

The mode of separation in HPLC is determined by the type of analyte, matrix and choice of mobile phase. The three basic techniques are reversed phase (where a non-polar stationary phase is used in conjunction with a polar eluent), normal phase (where the stationary phase has the higher polarity and a non-polar eluent is used) and ion exchange (where packing materials are utilized which contain charged functional groups and the eluent is usually buffered). In addition to these standard techniques there are HPLC separations based on size exclusion (cf. gel permeation), micellar separation and ion pair chromatography.

Reversed phase chromatography is generally recognized as the standard method of separation for HPLC, which probably contributed to its common use in early reported work. Reversed phase columns tend to be based around alkyl groups bound to a silica support material, the length of alkyl chain being denoted by, for example, C-9 for a nonyl group. The first reported application of HPLC to organotin analysis was by Brinckman who combined C-2 and C-18 columns with GF-AAS to analyse TPhT, TBT and tripropyltin with a 100% methanol mobile phase [19]. Early methods for reversed phase separation tended to use poorly suited detectors for environmental analysis and as a consequence poor or no detection limits are reported [15]. More recent work with ICP-MS detection has given sub-nanogram detection limits for the butyltins. An example of the separation which can be achieved with the reversed phase columns is shown by Kadokami who separated mono-, di- and trisubstituted methyl, butyl and phenyltin compounds [34]. Peak symmetry has been seen to improve with the addition of either tropolone or oxine. This is thought to reduce unfavourable column interactions, particularly for the monosubstituted compounds. The addition of 0.2% (m/v) to a THF (54% v/v), water (38% v/v) and acetic acid (8% v/v) mobile phase allows the separation of eight organotin compounds in 10 min with adequate resolution [35].

Normal phase separation is less common than reversed phase and consequently there are fewer papers reporting the use of these columns. These columns are also based on silica supports with organic substituents, but the organic groups are usually polar, e.g. cyanopropyl. The addition of morin in the place of tropolone to reduce column interaction led to the use of fluorescence detection with normal phase separation in the first reported

technique [36]. This separated various disubstituted organotin compounds, with detection limits in the sub-nanogram range. In the most recent report of normal phase separation, Astruc *et al.* used a toluene (100–95% v/v) and methanol (0–5% v/v) gradient to separate the butyltins, with a tropolone additive at trace levels (0.005% m/v) [37]. However, the monosubstituted compound was severely bound to the column and the technique caused marked degradation to the column.

Ion exchange is probably the most successful recent method to separate organotins by HPLC. There are two types of ion exchange, cation and anion, which define the chemical nature of the stationary phase, the support being usually silica or a styrene-based resin. The resin-based columns work over the whole of the pH range but they suffer swelling when subjected to an aqueous mobile phase. Solutions exist but are not ideal; for example the alternative silica-based packing solves this problem, but is not as flexible in its chemical properties, and is restricted to a pH range of 2–8. Silica is still favoured because of its stability at high pressures, when the swollen resin-based columns can be compressed.

The mobile phase is very important in ion exchange chromatography as it must be buffered to maintain an ionic equilibrium in the column. The main component is usually methanol/water and a salt, commonly ammonium acetate or citrate. The chromatography of the mono-substituted species is problematic at low methanol concentrations (<30%); at this point an acetic acid modifier is added to elute the species which are strongly bound to the column [15].

The first reported separation of organotin compounds with ion exchange chromatography is again by Brinckman. In 1981 he separated a variety of tri-substituted alkyltins on a cation exchange column [38]. This separation was ground-breaking for two reasons, namely the use of element-specific detection and the mechanism which was postulated as a result. To overcome the problems of poor sensitivity and selectivity of conventional detectors, GF-AAS was used. The suggested mechanism of separation was based on reverse phase interactions with the bonded phase, sulphonate cation exchange and interactions with the silanol sites.

More recent work has produced little variation in the composition of the mobile phase or the type of column, but a large number of detection systems have been used. These include fluorescence [39, 40], based on post-column reaction, ICP-MS [41, 42, 43] and ICP-AES [43]. The use of ion exchange as a method for the separation of organotins is now well established and over a third of the reported HPLC methods in a recent review utilize this form of column [15]. The most recent addition to our understanding of the separation came in 1993 when Pannier confirmed earlier theories about reversed phase interactions [110]. The work suggests that ion exchange is only partially responsible for the partitioning, and some reversed phase interaction as well as adsorption is involved.

The general development of liquid chromatography has seen the origin of separation techniques based on more esoteric principles such as size exclusion chromatography, ion pair and micelle-based separation. There are also two other separations which are not standard LC methods, supercritical chromatography and capillary electrophoresis, and they merit inclusion here.

Size exclusion chromatography (cf. gel permeation) separates analytes by the size of the molecule. The stationary phase has a porous surface and the physical size of the analyte influences the retention in the pores. Large molecules tend to remain in the mobile phase, whereas smaller molecules are absorbed into the pores, achieving an equilibrium analogous to that obtained by a chemical adsorption. The columns can be based on both silica and styrene polymers; for organotin analysis the reported method used the polymer forms. Columns of different pore sizes may be used in series to provide more adequate separation. In organotin analysis, size exclusion techniques have been used for the organotin-containing polymers used in antifouling coatings [20, 21]. Using these techniques, analysis of the polymers has been possible but no reported environmental analysis exists.

Micelle- and vesicle-based separations utilize surfactant properties. Varying levels of interaction with these surfactant forms provides the separation. Micelle separation has been used to good effect on standards of methyltins and trisubstituted ethyl- and propyltins. Sodium dodecylsulphate was used as the surfactant, and good detection limits and separation were achieved (absolute 25–100 pg as Sn for methyltins) [44]. One example of vesicle chromatography is reported, i.e. the separation of butyltins with a dihexadecyl phosphate vesicle system [45]. The success of this has been limited, which is thought to be due to the hydrophobicity of the butyltins.

Ion pair chromatography can be used to separate ionizable or ionized compounds; the ion pair is completed by the solute ion and a counterion. Organotin analysis uses reversed-phase ion pair separation, but the mechanism of separation is still not established. Separations are reported for both methyltins and trisubstituted alkyltins and published methods have relied on ICP-MS for much of the quantitative work. Tributyltin, among other alkyltins, has been determined using a C-18 column with a mobile phase consisting of methanol (80% v/v), water (19% v/v) and acetic acid (1% v/v) [43]. The ion pair is achieved through the addition of a reagent, in this case sodium pentanesulphonate. This system gave detection limits of 0.7 ng as Sn for TBT. Further work on environmental samples (fish tissue) with a styrene-based column and a similar mobile phase to the above gave detection limit improvements of over two orders of magnitude (2 pg as Sn for TBT) [46].

Supercritical fluids are gases compressed by a combination of pressure and temperature to such an extent that they have liquid properties as well as gaseous properties. They can 'dissolve' other species and can be used as a mobile phase in chromatography. They have some advantages over both gas

and liquid chromatographies. In gas chromatography, there is easy interfacing to the detector and little background interference from the mobile phase; however the analytes are not restricted to volatile and thermally stable compounds due to the liquid properties of the mobile phase. The problem of large mobile phase volumes from LC is also eliminated, and with it the difficult interfacing. Supercritical fluids are not without problems, as the high pressure requires specialized equipment.

The gas normally used for supercritical fluid chromatography (SFC) is CO_2 ; an additive is occasionally required for better solvation of the target analyte. Caruso reports separation of TBT and tetraphenyltin using CO_2 SFC, with the detection limits far exceeding any other technique at 0.043 pg as Sn for TBT [47]. However, coelution of DBT and TBT and TeMT meant that this system was not appropriate for analysis with complex environmental samples. Follow-up work by the same group separated tri- and tetra-substituted butyl- and phenyltin compounds, with very low absolute detection limits (0.2–0.8 pg as Sn) [48]. This work also examined optimization parameters for the separation. Further developments of the system by another group have produced an improved SFC–ICP interface, lowering detection limits tenfold.

The final liquid chromatography-based technique, the modified capillary electrophoresis (CE) technique, is micellar electrokinetic chromatography (MEKC). CE utilizes the separation of analytes relative to charge; MEKC is a variation on this technique which involves a surfactant additive, in this case sodium dodecylsulphate. This attempts to eliminate some of the unwanted interactions with the stationary phase in HPLC. Good separation is achieved between TMT and TBT with TBT eluting after 15 min [49, 50]. This analysis time could be lowered, but this piece of work was aimed at a mixture of organotin and organolead compounds. TBT was the most hydrophobic species analysed and hence had a long retention time. Absolute detection limits for this technique are 15.5 pg for TBT and 42.1 pg for TMT. As this is the first reported use of this technique, the reported detection limits appear to show promise for environmental analysis when used in conjunction with a suitable extraction system.

Table 15.3 summarizes recent examples of the direct techniques which are listed above.

15.3.3 *Indirect techniques*

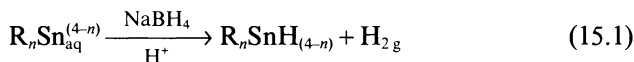
Indirect techniques involve the derivatization of the analyte to a volatile form which allows analysis free of matrix interference. It also allows simpler preconcentration techniques and simple separation by GC.

Any discussion of these methods requires a review of derivatization techniques, which fall into two different categories, hydride generation and alkylation. Many metals and organometallics are able to form volatile hydrides

Table 15.3 Direct methods for the analysis of organotin compounds

Instrument	Mode of separation	Conditions, column/mobile phase	Sample detected/ matrix (detection limits ng g ⁻¹ Sn)	Ref.
HPLC-UV/GFAAS	Reversed phase	Lichrosorb C ₁₈ /methanol (100%)	TPhT (166-UV)	19
HPLC-GFAAS	Normal phase	Nucleosil, cyanopropyl-bonded silica/toluene (100%) + (tropolone, 0.005%)	MBT, DBT, TBT/water and sediment (-)	37
HPLC-ICP-MS	Ion exchange	Partisil SCX/methanol (60%), ammonium citrate, pH 6 (0.18 M)	DBT, TBT/harbour sediment, PACS-1 SRM (0.04, TBT)	41
HPLC-RI/UV/GFAAS	Size exclusion	μ-Styragel (pore size 10 ² Å), tetrahydrofuran (100%)	TBT methacrylate (-)	21
HPLC-ICP-MS	Ion pair	PRP-1, poly(styrenedivinylbenzene)/methanol (94%), water (5%), acetate buffer (1%)	TMT, TBT, TPhT (0.002)	46

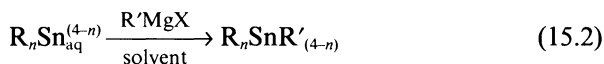
by reaction with sodium borohydride in aqueous acidic conditions according to the following reaction (eqn 15.1):



$$n = 1, 2, 3 \quad \text{R} = \text{organic (i.e. C}_4\text{H}_9\text{)}$$

Commonly the volatile hydrides are purged from the solution by an inert carrier gas to a packed cryogenic trap where preconcentration is achieved. The column is then flash heated and the analytes elute from the trap (which acts as a GC column), according to boiling points. The analytes are then passed to a sensitive and often element-specific detection system [17]. This derivatization has been used to great effect in a number of analyses with diverse instrumentation and differing environmental matrices, but there are however some interferences to the reaction caused by sulphur-containing samples which include environmental sediments and soils [51].

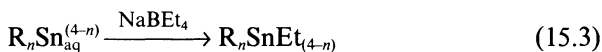
The alternative derivatization is to form alkylated derivatives, for which there are two methods. The most common method of alkylation is performed by the Grignard reaction to form ethylated and pentylated organotins according to the following reaction (eqn 15.2):



$$n = 1, 2, 3 \quad \text{R} = \text{organic (i.e. C}_4\text{H}_9\text{)}$$

This is a well defined synthetic route and is used in the synthesis of many compounds. However, it is complicated by the need for a water-free sample for reaction. Grignard derivatization for environmental samples usually involves three steps, acidification of sample, solvent extraction and then reaction. This is somewhat at odds with the prime aim of environmental sampling, which is to preserve the content and composition of the sample. This is usually done by reducing sample treatment to a minimum, which is not the case with Grignard methods. However, this method, like hydride generation, has been used to analyse environmental samples with success. The analysis of the extract is usually by GC combined with an element-specific detector.

The complexity of the Grignard alkylation led to an alternative method of alkylation which utilizes sodium tetraethylborate [51]. This compound works in a similar way to sodium borohydride, and reduces sample preparation compared with Grignard preparations. The reaction is given in eqn 15.3.



$$n = 1, 2, 3 \quad \text{R} = \text{organic (i.e. C}_4\text{H}_9\text{)}$$

This method was designed to simplify the alkylation method of derivatization, which is complex by the Grignard route. Applied to many organometallic species in the environment, this extension to organotin compounds has provided a method to volatilize environmental samples without the complexity of the Grignard reaction or the interferences of hydride generation. The volatile ethylated derivatives can be purged from solution into cryogenic traps or, if an organic solvent extraction is performed, direct injection of the ethylated species is possible. The ethylation reaction can also be used *in situ* without prior extraction [52].

Most of the indirect techniques utilize GC or purge and trap separation, and these techniques are best divided by the detection system used. The majority of detection utilizes element-specific apparatus such as AAS, AES and tin-specific flame photometric detection, though there is some use of MS and ICP-MS [6]. These detectors are also compatible with the form of sample presented by volatilization.

There has been only limited use of atomic absorption spectroscopy in direct techniques as flame atomization lacks sensitivity, and electrothermal atomization cannot handle the large amounts of mobile phase. The development of quartz furnace atomization, a form of electrothermal atomization, has allowed sensitive speciation of many organotin and other compounds in the environment [53]. The use of cryogenic trapping to preconcentrate analytes allows the trace amounts of organotin pollutants to be detected in a very simple system. The cryo-trap is also often used as a chromatography column, providing a simple purge and trap chromatography system, with hydride and ethylation used as a derivatization method [52].

The increase in sensitivity achieved with this technique is due to the combination of the preconcentration and the lack of background interference. The volatile compound is delivered to the furnace and instrument with very little matrix or interfering compounds present, aided by the element-specific nature of this technique where co-eluting contaminants may affect the analyte.

Quartz furnace atomic absorption spectrometry has been combined with hydride generation to analyse a number of environmental water samples. The conditions vary little in these techniques; a NaBH_4 solution with various acids added to lower the pH is used with a liquid nitrogen trap consisting of a packed U-tube [54–56]. The packing for the U-tube is usually a standard packed column support such as Chromasorb coated with various stationary phases, but glass wool has also been used [53]. The compounds separated and detected with these systems are the butyl-, methyl- and ethyltins, but detection limits vary. An early technique using glass wool trapping detected a huge number of tin compounds from lake water, seawater and algae with detection limits between 4 and 10 ng l^{-1} as Sn for water-based samples and $0.4\text{--}1 \text{ ng g}^{-1}$ in the algal samples. Later work with HCl/HNO_3 replacing the acetic acid in the reaction and utilizing a Chromosorb-W, 3% SP2100 packing gave detec-

tion limits for methyl- and butyltins in the range $0.2\text{--}2\text{ ng l}^{-1}$ as Sn [57–59]. One of these papers details the analysis for sediments which achieve detection limits of $0.07\text{--}0.1\text{ ng g}^{-1}$ as Sn [59]. Similar results have been obtained in seawater samples with OV-101 packing, for both seawater and sediments samples [60, 61].

The analysis of sediments and biota has been successful with HG-CT(GC)-QFAAS, and the increasing significance of this analysis has resulted in a number of publications. Four papers covering biota and sediment describe similar methods, although the detection limits show less variability when an acetic acid extraction is used [62–65]. The acetic extracts give detection limits of $0.5\text{--}2.0\text{ ng g}^{-1}$ as Sn for methyl- and butyltin compounds [62, 63], but for methanolic HCl limits of $1.8\text{--}8.8\text{ ng g}^{-1}$ as Sn were obtained [64, 65]. This demonstrates the importance of careful selection of extraction techniques.

The use of QF-AAS in alkylation is not so prevalent, although there are techniques using ethylation [51, 66], butylation [67] (of methyltin compounds) and pentylation by Grignard reaction [68–71]. Butyltin compounds have been analysed from sewage using ethylation and a silica-coated column, however, high detection limits were reported (40 ng g^{-1} as Sn). Butylation of methyltins in natural water again suffered from a lack of sensitivity ($0.04\text{--}2\text{ }\mu\text{g l}^{-1}$ as Sn) compared with the hydride methods [67]. Grignard ethylation of sludge gave a better result with a coated silica column, achieving detection limits of 2 ng g^{-1} as Sn for the butyltins [72]. Pentylation of fish tissue gave acceptable results for TBT with a detection down to 5.5 ng g^{-1} [71]. For sediment the mono-, di- and tributyltins are also detected by pentylation at concentrations as low as 0.45 ng g^{-1} as Sn.

The alkylation technique best suited to QF-AAS is ethylation by NaBEt_4 . In a river sediment sample, TBT, DBT and MBT were detectable at $0.9\text{--}1.2\text{ ng g}^{-1}$. The methyltins were also analysed in this method, however the extraction of MBT was inefficient (29%) [73]. Although this is not specific to ethylation or QF-AAS, the extraction of MBT is problematic, leading to studies of this problem [74, 75]. Other organotin analysis with NaBEt_4 is performed on organic extracts, and hence is very important in the development of simplified techniques. Ashby and Craig and Branch *et al.* reported the technique for butyltin compounds as well as methyl-, phenyl- and cyclohexyltin compounds in sediments with QF-AAS detection [51, 66, 76].

The use of atomic emission spectroscopy as a GC detector for environmental analysis was limited by the ability to provide a good emission from the source. This has changed with the development of plasma torches as sources of emission. Microwave-induced plasma has also been used in this application in a number of publications. The combination of GC-MIP-AES has proved successful when combined with alkylation as a derivative method. Grignard reagents have been used to pentylate organotin compounds, and butyl- and methyltins have all been detected with detection limits of

0.05 ng g^{-1} in sediments and 0.2 ng l^{-1} in river water [77]. It has also been used to detect mono- and dibutyltin in potable water [78].

An American interlaboratory comparison study has been conducted on pentylation/GC-MIP-AES and has proved successful in identifying many environmentally significant organotin compounds [79]. Reasonable precision was observed and further work is under way.

The GC-MIP-AES system has also been used to great effect with ethylation by sodium tetraethylborate. Szpunar-Lobinski *et al.* determined sub- ng l^{-1} quantities of butyl- and phenyltins in river water with a semi-automated system [80]. Recent publications show that the GC-MIP-AES method has been applied, with a rapid microwave-assisted extraction system, for the analysis of environmental sediment and biomaterials containing organotin compounds. Detection limits have been reported as 2 ng g^{-1} for 0.2 g (dry) of sample [81, 82].

Tin-specific flame photometric detection systems for GC are widely reported in environmental organotin analysis. An FPD system consists of a hydrogen-air flame and an interference filter at 610 nm . This is intended to be specific for the SnH emission in the gas phase, and until recently all tin FPD analysis has used this wavelength, despite a more sensitive band at 390 nm which is thought to be from a quartz surface-induced tin emission. This system has been utilized extensively for environmentally significant organotin compounds, in a wide variety of matrices. The GC-FPD system is compatible with both hydride generation and alkylation [6].

An early example of the application of FPD to hydride generation utilized a purge and trap system for the detection of methyltins with detection limits of 0.01 ng l^{-1} as Sn in various water samples (sea, rain, lake, etc.) [83]. Methyl- and butyltins were detected on two similar systems in seawater samples with detection limits of 0.3 and 10 ng l^{-1} , respectively [84, 85]. Both packed GC and capillary GC have been used with FPD detection for tin when combined with hydride generation. A Chromasorb OV-101 packed column [$2 \text{ mm} \times 6 \text{ ft}$ (1.8 m)] was used to separate DBT and TBT in seawater; detection limits of 2 ng l^{-1} were achieved [86, 87]. The capillary column ($0.32 \text{ mm} \times 25 \text{ m}$, 5% cross-linked phenyl methyl silicone) with the same sample and technique gave detection limits of 1 ng g^{-1} as Sn [87, 88]. The capillary technique was also used on a sediment and shellfish sample; a methanol/sodium hydroxide extraction matrix gave excellent recoveries ($>99\%$) with a limit of detection at 10 ng g^{-1} [88]. Hydride generation has also been used on butyltin compounds collected from the atmosphere, in which *c.* 20 m^3 of air was sampled using a Propak cartridge. Elution of the analytes was achieved with 0.3% HCl containing sodium borohydride; reported detection limits were 0.5 ng m^{-3} [89].

GC-FPD is more often utilized with alkylation by Grignard reagents; this is due to the compatibility with sample delivery. The Grignard reagent is dissolved in an organic solvent after the derivatization, and this is the most

common technique which uses a conventional GC injection of a solvent-based sample. This is balanced by the inherent problem of sample size with conventional GC, when less than 1 μl of sample is introduced from a sample of several millilitres. However, the sensitivity of the detector compensates for this shortfall and many groups have successfully utilized this technique for environmental analysis, but it should be noted that possible sulphur interferences have been investigated recently [90]. Tolosa and coworkers have reported detection of butyl- and phenyltin compounds in seawater, biota and sediment, where a capillary column is used following methylation by a Grignard reagent (LOD; seawater 0.5–3.5, biota 0.4–8.0 ng l^{-1}) [91, 92]. Supercritical fluid extraction has been used with Grignard ethylation for TBT with a short capillary (2.5 m) column based on a DB5 coating, but only TBT was detected from this sediment [93]. Several papers by Fent and Muller detail analysis of water samples such as rain water, waste water and fresh water, as well as sediment, fish and mussel tissue, using a tropolone diethyl ether extraction followed by ethylation with ethylmagnesium bromide. These samples were analysed for butyl-, phenyl- and cyclohexyltins [94–96]. In addition to these techniques, both propylation and pentylation are reported for environmental tin compounds [97–100]. A recent review covers more of these techniques [6].

There are few reports of GC-FPD combined with ethylation by sodium tetraethylborate, however recent papers report the use of this combination. The relative simplicity compared to Grignard derivatization has obvious advantages. A combined ethylation/extraction can be achieved in a one flask set up as reported by Astruc and coworkers [101] and Choi *et al.* [102]. Seawater analysis by Choi shows good linearity and LOD values of 4–12 ng l^{-1} as Sn are reported. Astruc demonstrates a greater linear range and also lower detection limits (0–400 ng l^{-1} and 0.4–2.1 ng l^{-1} , respectively). The above system was used for butyltins (both groups of workers) and phenyltins (Astruc).

As mentioned previously, another tin emission band is available for use at 390 nm. This band originates from a quartz surface-induced emission as opposed to the normal band which is a gas phase emission. In theory this band is up to 1000 times more sensitive for tin, however in practice the improvements are less dramatic. This development of FPD has only recently been applied to tin analysis; limits of detection for butyltin species have been reported at 5, 18 and 2 pg for MBT, DBT, TBT, respectively [103]. This has also been applied to phenyl- and butyltin compounds, showing detection down to 0.7 pg [104].

The final significant detection system for indirect techniques is mass spectroscopy. The coupling of GC to mass spectroscopy is well known, but not well used in this area, probably due to the advantages of element-specific detection. GC-MS is reported for methylated Grignard derivatives from seawater and also mussel [105, 106], but these methods give significantly higher

detection limits than the element-specific equivalents. However, the use of ICP as an ion source for MS gives improved detection limits but loses the absolute identification given by MS. A recent overview on the application of this technique to environmental organometallics has been published [107]. The specific application of GC-ICP-MS to organotin compounds is not widely reported. The development of two GC-ICP interfaces has been reported and the systems were tested using organotin compounds [108, 109]. One system uses a sediment sample and direct ethylation using NABEt₄, which proved to be an acceptable system for environmental analysis [109].

Table 15.4 summarizes indirect methods for the analysis of organotin compounds.

15.4 Conclusion

There is a wide variety of analysis methodology for environmental organotin compounds which has been developed over the past 20 years. The increasing significance of TBT pollution is reflected in its impact on the marine food chain, which has led to this expansive development. There is now such a range of methods it is difficult to specify at first sight a method for a particular analyte or environmental matrix. An element of personal preference is involved as well as of available equipment. The cost or age of equipment may not be a factor in organotin analysis, as an older AA-based technique is often as sensitive as a tin-specific FPD and often more so than an expensive GC-MS. As with all environmental analysis, good design of the experiment and sampling are essential; poor quality in either of these areas will invalidate the most sensitive analysis.

Abbreviations

AAS	Atomic absorption spectrometry	GF	Graphite furnace
AES	Atomic emission spectrometry	HG	Hydride generation
AFS	Atomic fluorescence spectrometry	HPLC	High performance liquid chromatography
CE	Capillary electrophoresis	ICP	Inductively coupled plasma
CNS	Central nervous system	LC	Liquid chromatography
CT	Cryogenic trap	LOD	Limit of detection
DBT	Dibutyltin	MBT	Monobutyltin
FPD	Flame photometric detector	MEKC	Micellar electrokinetic chromatography
GC	Gas chromatography	MIP	Microwave induced plasma

Table 15.4 Indirect methods for the analysis of organotin compounds

Instrument	Extraction/derivatization	Sample detected/ matrix (detection limits ng g ⁻¹ Sn)	Ref.
HG-CT-QFAAS	None/hydride generation (NaBH ₄) pH 5	DBT, TBT/seawater (2 ng l ⁻¹)	54
GC-QFAAS	HCl, NaCl (toluene)/ethylation (Grignard, EtMgBr)	MBT, DBT, TBT/sewage sludge (40 ng l ⁻¹ liquid, 2 ng l ⁻¹ dry solid)	72
GC-MIP-AES	Acetic acid, water, DDTC in pentane (hexane/isooctane)/pentylation (PeMgBr)	MMT, DMT, TMT, MBT, DBT, TBT/sediment (0.05)	77
HG-CT-FPD	None/hydride generation (NaBH ₄) pH 2	MMT, DMT, TMT, MBT, DBT, TBT/seawater (0.3)	84
GC-FPD	HCl, tropolone diethyl ether/ethylation (Grignard, EtMgBr)	MBT, DBT, TBT, MPhT, DPhT, TPhT/sediment (0.05–2), mussel (9–23)	94-96
GC-MS	HBr, tropolone, benzene/methylation (MeMgBr)	MBT, DBT, TBT/seawater (10 mg l ⁻¹)	105
GC-ICP-MS	None/ <i>in situ</i> ethylation (NaBEt ₄)	—/sediment	109

MS	Mass spectrometry	SFC	Supercritical fluid chromatography
NaBEt ₄	Sodium tetraethylborate		
NaBH ₄	Sodium borohydride	TBT	Tributyltin
nm	Nanometer	TeMT	Tetramethyltin
QFAAS	Quartz furnace atomic absorption spectrometry	TMT	Trimethyltin
		TPhT	Triphenyltin
R	Alkyl group	UV	Ultraviolet

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